TRANSPORT PROCESSES IN ANION EXCHANGE MEMBRANES

A thesis presented for the degree of Ph.D.

by

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SUMMARY

This thesis constitutes a study of transport processes in A.M.F. A-104 anion exchange membranes. Measurements were made on five different systems: the membrane equilibrated with 0.1, 0.5, 1.0 and 2.0 molar sodium chloride and 0.1 molar sodium iodide. For each system the concentrations of the mobile species - counterion, coion and water - and the membrane fixed charged groups were determined, and measurements were made of the self diffusion coefficients of all the mobile species, coion and counterion transport numbers and the water transference number. Osmotic flows were obtained with 0.15/0.05 and 1.5/0.5 molal sodium chloride and 0.15/0.05 molal sodium iodide concentration gradients while salt flows across the membrane were measured in the two sodium chloride concentration cells. Membrane conductivity measurements were made in the 0.1 and 1.0 molar sodium chloride and 0.1 molar sodium iodide systems. General trends and features in the results of the individual transport experiments have been discussed and, where appropriate, comparisons have been made with the results of other workers in other membrane systems.

Combination of the results of the transport experiment results permits a complete analysis of the membrane processes in terms of non equilibrium thermodynamics. This approach, which yields a set of characteristic phenomenological coefficients for the membrane at a given concentration, requires the performance of six independent transport experiments at that concentration, whereas under isothermal, isobaric conditions the maximum possible is five (conductivity, transport numbers, water

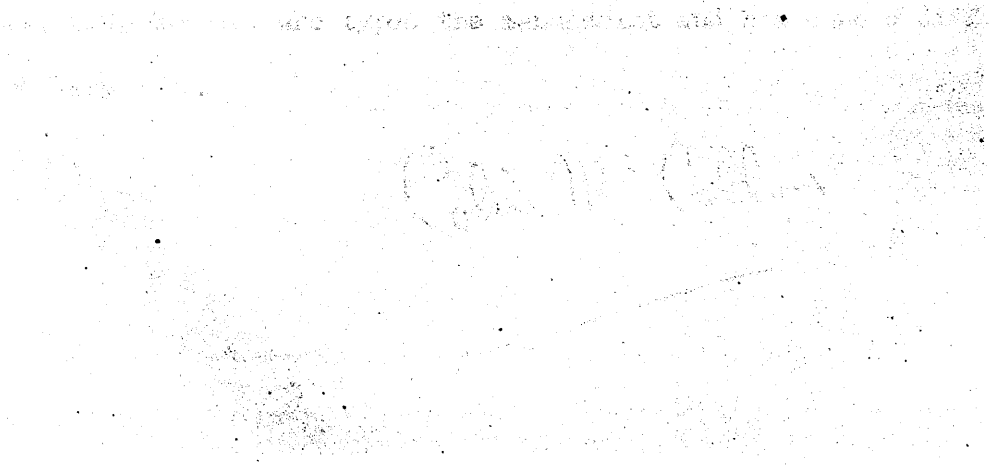
transference number, salt and osmotic flows). To solve the matrix of coefficients, therefore, requires a specific assumption about the behaviour of species in the membrane. A number of plausible assumptions have been subjected to critical examination both from a theoretical standpoint and from the intercomparison of the resulting sets of coefficients calculated for the 0.1 and 1.0 molar sodium chloride systems. The iodide form was treated as a binary system rather than a ternary as the coion was present in sufficiently low concentrations as to be negligible.

The phenomenological coefficients were obtained both as mobility (ℓ) coefficients, (when the flows are expressed as linear combinations of the forces) and as resistance or frictional (R) coefficients (when the forces are expressed as linear combinations of the flows). The magnitudes and signs of the coefficients have been discussed at some length in an attempt to clarify the behaviour of the separate species in the membrane. The properties of the iodide form appear to be dominated by a strong interaction between the quaternary ammonium fixed group and the iodide ion and this appears plainly in the phenomenological coefficients. The matrix-counterion interaction in the chloride form is much less important but nonetheless seems to be significantly larger than the matrix-counterion interaction in a polystyrene sulphonate cation exchanger in the sodium form.

In common with recent work on cation exchange membranes, the isotope-isotope frictional coefficients of the counterions have been observed to be both large and have the opposite sign to that which would be expected on theoretical grounds. An attempt to explain the phenomenon has been made.

The structure of the membrane has been investigated using coion uptake and permeability data to calculate the parameters of the Glueckauf theory and the results have been compared with electron micrographs of sections of the membrane taken in the chromate and chloride forms.

A short study of membrane selectivity was carried out using sodium chloride/iodide solutions of overall ionic strength 0.1 molar. The results confirmed the strong preference of the membrane for the iodide ion inferred from the transport results and the rational thermodynamic equilibrium constant and free energy of ion exchange in the chloride/iodide system were calculated.



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CHAPTER 1 INTRODUCTION

1.1 Background and Aims

Synthetic ion exchange membranes are a relatively recent development. The first patent dates from the early 1950's and good, thin, strong membranes have only been available commercially for about ten years. Since then however they have been put to ever increasing use technologically, particularly in desalination by electrodialysis and reverse osmosis. Unlike natural, biological membranes, synthetic membranes offer a relatively simple, controllable system for study, and elucidation of their behaviour may well be an important step towards understanding the complex biological membrane. If an ion exchange membrane - and from now this will be taken to refer to a synthetic ion exchange membrane - is allowed to come to equilibrium with a solution of a single electrolyte, four separate species may be distinguished in the membrane phase. These are counterion, coion, solvent (usually water) and the matrix, including the fixed charge. The counterions have the opposite charge sign to the fixed charges and coions, and depending on the sign of the fixed charges, the membrane may be either a cation or an anion exchanger. The general principles of ion exchange do not require elaboration here and reference may be made to Helfferich's excellent textbook on the subject (1) ±.

± References in the introduction and, where required, in the appendices will be found at the end of these sections. All other references are collected in the main bibliography.

Most work on ion exchange systems has been done on cation exchangers, yet in many ways anion exchange is the more interesting as the fixed charged group is usually of the quaternary ammonium type and this is known to interact with low charged anions and water in an unusual way (Section 1.3). In the work presented here attention will principally be directed at the transport properties of an anion exchange membrane. To measure these properties it is necessary to apply a known force to the membrane and measure the resultant flows of the mobile species. At the outset it was decided to restrict the system to isobaric, isothermal conditions to avoid the experimental difficulties which arise when pressure and temperature gradients are employed as thermodynamic forces (2)(3). Under these conditions the independent transport experiments are conductivity, transport numbers of coion and counterion, electroosmotic flow, osmotic flow and salt flow. The theoretical description of membrane transport processes, the subject of Chapter 2, is fairly advanced but lacks extensive experimental confirmation. A rigorous description is given by non equilibrium thermodynamics which yields a set of characteristic phenomenological coefficients but there is then the problem of their interpretation. Nonetheless the non equilibrium thermodynamic description is superior to all the others in their present state of development. The complete solution of the phenomenological coefficients does have a practical drawback in that as the number of mobile species inside the membrane increases, the number of independent experiments required to characterise a system rapidly becomes very large. For a membrane in equilibrium with a single electrolyte the

number of independent experiments is six, one more than those possible under isobaric, isothermal conditions. The complete solution of the phenomenological coefficients for this system, the major aim of the work, therefore required that an assumption be made about it, and so another aim was the critical evaluation of some of the more plausible ones. It may be considered that self diffusion experiments which are after all independent transport experiments, provide the sixth experiment but there is the extra complication of isotope-isotope interactions (discussed in Chapters 2 and 5) and the use of these experiments requires an assumption about its magnitude. For some time it was thought that isotope-isotope interactions were negligible for the mobile ionic species, but recent work has shown that it is not the case for the counterion (4)(5). Even more interesting has been the observation that the sign of the counterion isotope-isotope frictional coefficient appears to be opposite to what might have been expected. It was hoped to investigate this phenomenon further in the course of the work.

The systems chosen to study were an anion exchange membrane (section 1.2) in equilibrium with aqueous solutions of sodium chloride and sodium iodide. The iodide form was chosen because of the strong possibility of ion pairing which should be reflected in the magnitudes and signs of the phenomenological coefficients. Some ion pairing may also be present in the chloride form, although solution data suggests that this is less likely (section 1.3). There are no sets of phenomenological coefficients for anion exchange systems yet

published but comparison is possible with those obtained for cation exchange systems (4)(5) where ion pairing appears to be negligible.

Another possibility for study is the effect of changing the external solution concentration on the transport properties and phenomenological coefficients, and to do this it was decided to collect a full set of data at two widely different sodium chloride concentrations (0.1 and 1.0 molar) and investigate selected properties at other concentrations.

1.2 The Membranes

The ion exchange membranes studied in this work were AMF - A104 anion exchange membranes manufactured and kindly supplied by the American Machine and Foundry Company, Springdale, Connecticut. Two slightly different methods of preparation of these membranes have appeared in the literature. The first, quoted by Helfferich(6) and Christensen (7), involves impregnating a polyethylene film with styrene or a styrene-divinylbenzene mixture and exposing it to cobalt-60 gamma radiation which grafts the styrene units to the polyethylene backbone. Crabtree and Glueckauf (8), however, differ in the grafting procedure, stating that it is chemically initiated with stannic chloride and that this method has superseded the irradiation technique. (These authors also say that the exchange groups are of the Dowex-2 type i.e. benzylethanoldimethylammonium). After grafting, the film is subjected to chloromethylation then amination with a tertiary amine to introduce one quaternary ammonium group per polystyrene unit. The graft-copolymer anion exchange membrane which results is quasi-homogeneous and has excellent

mechanical and electrochemical properties.

In the course of the work there was a slight experimental overlap with both Christensen and Crabtree and Glueckauf. If the different methods of preparation have caused differences in the properties then these should emerge, and possibly indicate which preparative method is relevant to the membranes used here.

1.3 Quaternary Ammonium-Halide Interactions

Unquestionably one of the most important factors in determining the behaviour, transport or otherwise, of anion exchangers of the type used in this work is the nature and magnitude of the interaction between the quaternary ammonium fixed ions and the halide counterions. As an ion exchange membrane is far from being the ideal system for studying these effects it is necessary to make a small diversion into solution studies to obtain some idea of what may be occurring within the exchanger phase. The aqueous solution behaviour of quaternary ammonium salts has for a long time been a subject of considerable interest and an extensive literature has accumulated. It is beyond the scope of this thesis to examine it in any great detail but in this section an attempt will be made to describe those aspects of the solution work relevant to the anion exchange system. The fundamental cause of the quaternary ammonium-halide interaction appears to be the interaction of the quaternary ammonium cation with water. Small or highly charged ions such as Li^+ and Mg^{2+} orientate and immobilise several layers of water molecules around them by strong ion-dipole attraction in their intense electrical fields, while larger low charged ions such as I^- and NO_3^-, being unable to

orientate water molecules, cause disruption of the water structure in their immediate vicinity (9). Beyond this again come the large organic ions like the quaternary ammonium cations where the charge is well shielded from the water by large hydrophobic alkyl groups. These ions in fact have many features in common with neutral molecules and it was through a study by Frank and Evans (10) on the entropy changes when hydrocarbons (the neutral, isoelectronic analogues of the quaternary ammonium cations) are dissolved in water, that modern ideas began to develop. To explain the decrease in entropy observed, these authors proposed that there was increased ordering of the water molecules round the dissolved hydrocarbon molecules. The hydrophobic molecule does not attract or orientate the water molecules in the immediate vicinity as strongly as does the next shell of water molecules, with the result that the water molecules on the internal surface of the cavity surrounding the hydrocarbon molecule are more firmly coordinated into the bulk water structure. There is thus an overall increase in order and decrease in entropy in the system. The free energy or 'escaping tendency' of the hydrocarbon is increased, which explains in thermodynamic terms the reluctance of these compounds to dissolve in water, and the larger the hydrocarbon the larger all the effects become. Similar behaviour would be expected from the large, non-polar quaternary ammonium ions and indeed the activity and osmotic coefficients of the simple symmetrical tetraalkylammonium chlorides increase in the order $Me_4N^+ < Et_4N^+ < Pr_4N^+ < Bu_4N^+$ (11). The tetraalkylammonium iodides however display the opposite trend (11) and Diamond (12) has suggested that it is caused by the water forcing the hydrophobic cations and anions together to minimise the disturbance to the water structure. The extra

work required to force a hydrophobic anion into a pre-existing cavity containing a hydrophobic cation is less than that required to sustain two separate cavities. Ion pairing in the tetraalkylammonium iodides should also produce a drastic reduction in the activity coefficients and this has been observed (11)(13)(14). Of specific relevance to anion exchangers, Boyd, Schwarz and Lindenbaum (15) have measured the osmotic and mean molal activity coefficients of benzyltrimethylammonium and benzylethanoldimethylammonium chlorides and bromides - model compounds for strong base anion exchangers - and have found them appreciably smaller than the corresponding tetramethylammonium and choline salts. The implication of the above arguments is that water structure enforced ion pairing might occur in the membrane being studied, particularly in the iodide form. If the effect is important, then its recognition in the results will provide a major problem of interpretation.

REFERENCES

1. F. HELFFERICH, "Ion Exchange", McGraw-Hill, New York, 1962.
2. H. KRÄMER AND P. MEARES, Biophys. J. 9 1006 (1969).
3. N. LAKSHMINARAYANAIAH, Chem. Rev. 65 492 (1965).
4. E.M. SCATTERGOOD AND E.N. LIGHTFOOT, Trans. Faraday Soc. 64 1135 (1968).
5. C.R. GARDNER, Ph.D. Thesis, University of Glasgow, 1970.
6. Reference (1), p. 64.
7. E.L. CHRISTENSEN, Ph.D. Thesis, University of Wisconsin, 1968.
8. J.M. CRABTREE AND E. GLUECKAUF, Trans. Faraday Soc. 59 2639 (1963).
9. R.W. GURNEY, "Ionic Processes in Solution", McGraw-Hill, New York, 1953.
10. H.S. FRANK AND M.W. EVANS, J. Chem. Phys. 13 507 (1945).
11. S. LINDENBAUM AND G.E. BOYD, J. Phys. Chem. 68 911 (1964).
12. R.M. DIAMOND, J. Phys. Chem. 67 2513 (1963).
13. V.E. BOWER AND R.A. ROBINSON, Trans. Faraday Soc. 59 1717 (1963).
14. B.J. LEVIEN, Aust. J. Chem. 18 1161 (1965).
15. G.E. BOYD, A. SCHWARZ AND S. LINDENBAUM, J. Phys. Chem. 70 821 (1966).

CHAPTER 2

THEORETICAL DESCRIPTION OF MEMBRANE TRANSPORT PROCESSES

Current theoretical descriptions of membrane transport processes can be approximately classified under the headings of absolute rate theory, non equilibrium thermodynamics and the classical theories such as the Nernst-Planck.

The absolute reaction rate theory of Eyring and coworkers (1), where the membrane is considered as a series of potential energy barriers, has not been widely applied. The complexity of the equations has made this approach, so far, of little practical use and as such is not employed in this work. Nonetheless absolute reaction rate theory has proved to be conceptually very valuable in understanding the mechanisms of transport inside the membrane.

Non equilibrium thermodynamics (2)(3)(4)(5) is completely rigorous in its descriptions of membrane transport processes but it is essentially phenomenological and thus the physical interpretation of the coefficients requires the use of a model.

At the expense of ignoring diffusional coupling between mobile species, the extended Nernst-Planck flux equations (6) provide a predictive theory. Although these flux equations were originally developed to describe diffusional processes in ideal solutions, they have proved very successful when applied to membrane systems. In this chapter a nonequilibrium thermodynamic treatment is developed for the membrane transport processes under study.

Limited use is made of the Nernst-Planck equations to obtain equations for the electrical properties of a membrane, and comparisons are drawn between the non equilibrium thermodynamic and Nernst-Planck descriptions.

2.1 Non Equilibrium Thermodynamics

2.1.1 The Extension of Classical Thermodynamics

Classical thermodynamics concerns itself principally with the description of systems at equilibrium or undergoing reversible processes. At equilibrium the intensive parameters are completely determined by the extensive parameters and are independent of time and spatial coordinates. A system perturbed from equilibrium, and which therefore has at least one of its state parameters dependent on position, tends to decay irreversibly towards equilibrium. Non equilibrium thermodynamics attempts to describe this decay process in terms of the fluxes of extensive or capacitative quantities caused by the existence of gradients of intensive parameters as the system seeks to re-establish equilibrium. The thermodynamics of irreversible processes has therefore a kinetic element which is completely lacking in classical thermodynamics.

For an irreversible process, classical thermodynamics is not informative providing only the inequality

$$dS > 0 \qquad (2.1)$$

which states that for the system plus surroundings the overall entropy change is positive. It can be shown (7) that dS can be split into two terms, d_eS the entropy exchanged reversibly with the surroundings, and d_iS the entropy created by the irreversible processes occurring in the system.

$d_i S$ is thus positive definite for an irreversible process and zero for a reversible one.

If the rate of creation of entropy per unit volume per unit time is denoted by σ, then σ is related to the rate of creation of entropy in the system $d_i S/dt$ by

$$\int_V \sigma \, dV = \frac{d_i S}{dt} \qquad (2.2)$$

To evaluate σ it is necessary to make an important assumption (8) viz. that the Laws of Thermodynamics can be applied to very small volumes in the system even though irreversible processes are taking place in the system as a whole. This postulate of local equilibrium immediately imposes the restriction that the system cannot be very far from equilibrium (ie. the gradients of intensive parameters must not be steep).

For a system in which no chemical reactions are occurring it is then possible to evaluate σ in general as (8)

$$\sigma = \sum_{i=1}^{n} J_i' X_i' \qquad (2.3)$$

where X_i' is the force conjugate with the flow J_i' and the J_i' and X_i' are independent. If the flows are defined as that of heat, J_q, and those of matter J_j then equation 2.3 becomes

$$\sigma = J_q \cdot \operatorname{grad} \frac{1}{T} + \sum_{j=1}^{k} J_j \cdot \operatorname{grad} \left(\frac{-\tilde{u}_j}{T} \right) \qquad (2.3a)$$

where T is the absolute temperature and $\tilde{u}_j$ is the electrochemical potential of species j.

The choice of flows thus fixes the thermodynamic forces which have to be employed.

It is more usual however to define the dissipation function $\Phi = T\sigma$, where Φ measures the rate of local dissipation of free energy per unit time, whence equation 2.3 becomes

$$\Phi = \sum_{i=1}^{n} J_i X_i = J_s \cdot \text{grad}\,(-T) + \sum_{j=1}^{k} J_j \cdot \text{grad}\,(-\tilde{u}_j) \qquad (2.4)$$

where J_s is the entropy flow. Again the J_i and X_i must be independent. In this form the flows and forces take on more familiar forms. There is nonetheless a certain latitude in the choice of flows and forces, the criteria being that their product must have the dimensions of free energy per unit time and that any transformation of the J_i and X_i must leave the summation unchanged.

2.1.2 The Onsager Reciprocal Relations (O.R.R.)

To make practical use of equation 2.4 it is necessary to relate the J_i and X_i. The laws of Fourier, Fick and Ohm discovered in the first half of the nineteenth century had shown the linear dependence of a flow on its conjugate force while the later work of such people as Dufour, Soret and Peltier had shown that, for a sufficiently slow process, a flow could also linearly depend on a non conjugated force.

In 1931 Onsager (9)(10) proposed that for a slow process occurring not far from equilibrium, thermodynamic flows and forces were linearly related by a set of phenomenological equations which may be represented

$$J_i = \sum_{k=1}^{n} \ell_{ik} X_k \qquad (i = 1, 2.....n) \qquad (2.5)$$

where the ℓ_{ik} have the units of flow per unit force and can be considered as generalised conductances or permeabilities.

It is equally possible to write the forces in terms of the flows in which case the phenomenological equations become (11)

$$X_i = \sum_{k=1}^{n} R_{iK} J_K \quad (i=1, 2.....n) \qquad (2.6)$$

where the R_{iK} have the units of force per unit flow and can be regarded as generalised resistance or frictional coefficients.

The R_{iK} are related to the ℓ_{iK} by the equation

$$R_{iK} = \frac{|\ell_{iK}|}{|\ell|} \qquad (2.7)$$

where $|\ell_{iK}|$ is the minor of ℓ_{iK} and $|\ell|$ is the determinant of all ℓ coefficients.

For an n component system there would therefore be n^2 unknown phenomenological coefficients and consequently n^2 independent experiments would be required to determine them. Even with n = 3 the experimental analysis becomes extremely difficult. The fundamental discovery of Onsager (9), arising from the principle of microscopic reversibility, was that the ℓ coefficient matrix is symmetrical so that

$$\ell_{iK} = \ell_{Ki} \qquad (i \neq k) \qquad (2.8)$$

(and thus similarly $R_{iK} = R_{Ki} \quad (i \neq k) \qquad (2.8a)$)

Equations 2.8 and 2.8a are statements of the Onsager Reciprocal Relations (O.R.R.) and reduce the number of independent coefficients required to characterise the system from n^2 to $n(n+1)/2$.

Although there is a considerable lack of experimental data, the O.R.R. are justified to within experimental error (12) under a number of conditions which are far from the limitations imposed by the statistical mechanical treatment involving microscopic reversibility.

Using equation 2.4 in conjunction with the O.R.R. and the condition for overall positive entropy production, the further important conditions are obtained

$$\ell_{ii} \geq 0 \qquad (i=1,2....n) \qquad (2.9)$$

$$\ell_{ii} \cdot \ell_{kk} \geq (\ell_{ik})^2 \qquad (\text{ie } |\ell| \geq 0) \qquad (2.10)$$

with the analogous conditions in the frictional representation

$$R_{ii} \geq 0 \qquad (i=1, 2....n) \qquad (2.9a)$$

$$R_{ii} \cdot R_{kk} \geq (R_{ik})^2 \qquad (2.10a)$$

2.2 Application of Non Equilibrium Thermodynamics to Membrane Transport Processes

A number of treatments of membrane transport processes employing non equilibriu thermodynamics have appeared in the literature, (13)(14)(15)(16)(17)(18) using a variety of transformations of the flows and forces. The mobility coefficient approach used by Miller (19) to describe transport processes in binary electrolytes is particularly useful when applied to membranes since it leads to relatively simple equations.

Before embarking on a detailed examination, it is necessary to define the membrane systems more rigorously. Attention has been restricted to isobaric, isothermal systems. Since all forces and flows are measured normal to the membrane surfaces the thermodynamic forces reduce to the one dimensional negative gradients of electrochemical potential of the species in the membrane (since all irreversible processes are considered to take place in the membrane phase). These species are counterion (1), coion (2), solvent (water) (3) and matrix including fixed charge (4).

2.2.1 Mobility or ℓ Coefficient Approach

With the four components defined as above, equation 2.4 becomes

$$\Phi = T\sigma = \sum_{i=1}^{4} J_i X_i \qquad (2.11)$$

where the J_i are the mass fixed flows of matter in e.g. mole. cm^{-2} sec^{-1} and the X_i are the thermodynamic forces in joule. $mole^{-1}$ cm^{-1}.

For one dimensional flow in the x direction the X_i may be written

$$X_i = -\frac{\partial \tilde{u}_i}{\partial x} = -\frac{\partial u_i}{\partial x} - z_i F \frac{\partial \phi}{\partial x} \qquad (2.12)$$

where $\tilde{u}_i$ is the electrochemical potential in joule. $mole^{-1}$

u_i is the chemical potential

z_i is the signed valence of ion i

F is the Faraday in coulomb. $equivalent^{-1}$

ϕ is the electrical potential in volts

and x is expressed in cm.

The X_i, however, are not independent, but are related by the Gibbs-Duhem equation, $\sum_i n_i d\tilde{u}_i = 0$, where n_i is the number of moles of i, which may be written for this system

$$\sum_{i=1}^{4} c_i X_i = 0 \qquad (2.13)$$

At this stage it is desirable to transform the flows and forces by choosing a suitable frame of reference. The first, and most convenient, is an apparatus fixed frame of reference which is identical with that of the fixed membrane. The second, a solvent-fixed frame of reference, allows direct comparison with solution data. Mobility coefficients on the membrane fixed frame of reference will be denoted ℓ_{ij}.

Equations allowing the transformation from membrane fixed to solvent fixed coefficients and vice versa are given in Appendix A.1. Such solvent fixed phenomenological coefficients will be denoted L_{ij}. Equation 2.13 shows that the four forces are not independent and X_4 may be written in terms of the other three to eliminate it from equation 2.11. Rearranging, this becomes

$$T\sigma = \sum_{i=1}^{3} (J_i - (c_i/c_4).J_4)\, X_i$$

$$= \sum_{i=1}^{3} J_i^* X_i \qquad (2.14)$$

where J_i^* is the membrane fixed flow of species i. This transformation satisfies the conditions of section 2.1.1 and also preserves the O.R.R. For convenience the asterisk will now be dropped from equation 2.14, it being understood that J_i will refer to a membrane fixed frame of reference for the remainder of this section. Solution of the ℓ_{ij} coefficient matrix requires the performance of six independent experiments. The theoretical treatment of those available from electrical and chemical potential forces under steady state conditions will now be considered.

Electrical Potential Gradient Only

There are three experiments, namely, conductivity, transport number and electroosmosis, in which the external applied force is electrical potential gradient alone. The solutions on either side of the membrane in these experiments are identical so that there are no chemical potential gradients across the membrane. In these cases

$$X_i = -\frac{\partial \tilde{u}_i}{\partial x} = -z_i F\left(-\frac{\partial \phi}{\partial x}\right) \qquad i=1,\ 2 \qquad (2.15)$$

and $X_3 = 0$ (3 is an uncharged species) (2.16)

The phenomenological equations become

$$J_1 = \ell_{11} X_1 + \ell_{12} X_2 \qquad (2.17a)$$

$$J_2 = \ell_{21} X_1 + \ell_{22} X_2 \qquad (2.17b)$$

$$J_3 = \ell_{31} X_1 + \ell_{32} X_2 \qquad (2.17c)$$

2.2.1.1 Conductivity

When an electric current is passed through the membrane the current density in amp cm^{-2} is given by

$$I = (z_1 J_1 + z_2 J_2).F \qquad (2.18)$$

Substituting for J_1 and J_2 from equations 2.17a and 2.17b and using equation 2.15 for X_1 and X_2, equation 2.18 becomes

$$I = F^2 . -\frac{\partial \phi}{\partial x} (z_1^2 \ell_{11} + 2z_1 z_2 \ell_{12} + z_2^2 \ell_{22}) \qquad (2.19)$$

Ohm's law states that

$$I = \bar{K} \left(-\frac{\partial \phi}{\partial x} \right) \qquad (2.20)$$

and provided the ℓ coefficients remain constant throughout the experiment, the substitution of equation 2.20 into equation 2.19 yields

$$\bar{K} = F^2 \lambda \qquad (2.21)$$

where $$\lambda = (z_1^2 \ell_{11} + 2z_1 z_2 \ell_{12} + z_2^2 \ell_{22}) \qquad (2.22)$$

2.2.1.2 Transport Number

The transport number, t_i, of an ion on a given frame of reference is defined as the fraction of the total current carried by that ion and can thus be written

$$t_i = \frac{z_i F J_i}{I} \qquad (2.23)$$

For ion 1 therefore, substituting for I by equation 2.18 and for J_1 and J_2 by equations 2.17a and 2.17b and finally for X_1 and X_2 by equation 2.15.

$$t_1 = (z_1^2 \ell_{11} + z_1 z_2 \ell_{12})/\Delta \qquad (2.24a)$$

and similarly

$$t_2 = (z_2^2 \ell_{22} + z_1 z_2 \ell_{12})/\Delta \qquad (2.24b)$$

2.2.13 Electroosmosis

The transference number of a species is defined (20) as the number of moles of the species transferred by one Faraday of electricity through a stationary cross section in the direction of positive current, i.e. in this case

$$t_3 = \frac{J_3 F}{I} \qquad (2.25)$$

and similarly as above

$$t_3 = (z_1 \ell_{13} + z_2 \ell_{23})/\Delta \qquad (2.26)$$

Experiments Conducted with a Chemical Potential Gradient

If a membrane is placed between two solutions of the same electrolyte at different concentrations then diffusion of solute and solvent will occur, with the consequent setting up of a diffusion potential, as the system seeks to establish equilibrium. The use of concentration gradients to obtain membrane phase ℓ or R coefficients is open to the fundamental objection that these coefficients are functions of the intensive parameters such as concentration, so that salt and osmotic flow experiments will in reality provide average values of the coefficients. The only way of overcoming this is to ensure that the gradients are as small as possible, in which case the phenomenological coefficients should not vary significantly from one side of the membrane to the other.

The thermodynamic forces become

$$X_i = \left(-\frac{\partial \tilde{u}_i}{\partial x}\right) = \left(-\frac{\partial u_i}{\partial x}\right) + z_i F\left(-\frac{\partial \phi}{\partial x}\right) \quad i=1,2 \qquad (2.27)$$

and $$X_3 = \left(-\frac{\partial u_3}{\partial x}\right) \qquad (2.28)$$

In this system there is no net transfer of charge and thus

$$I = (z_1 J_1 + z_2 J_2).F = 0$$

The phenomenological equations are

$$J_1 = \ell_{11} X_1 + \ell_{12} X_2 + \ell_{13} X_3 \qquad (2.29a)$$

$$J_2 = \ell_{21} X_1 + \ell_{22} X_2 + \ell_{23} X_3 \qquad (2.29b)$$

$$J_3 = \ell_{31} X_1 + \ell_{32} X_2 + \ell_{33} X_3 \qquad (2.29c)$$

Substitution of equations 2.29a and 2.29b into the zero current condition gives

$$(z_1 \ell_{11} + z_2 \ell_{12})X_1 + (z_1 \ell_{12} + z_2 \ell_{22})X_2 + (z_1 \ell_{13} + z_2 \ell_{23})X_3 = 0$$

which from equations 2.24a, 2.24b and 2.26, can be put in the form

$$t_1/z_1 . X_1 + t_2/z_2 . X_2 + t_3 X_3 = 0 \qquad (2.30)$$

Further expansion of the X_i according to equations 2.27 and 2.28 then gives the identity

$$F.\left(-\frac{\partial \phi}{\partial x}\right) = \frac{t_1}{z_1 . \partial x}\frac{\partial \tilde{u}_1}{} + \frac{t_2}{z_2 . \partial x}\frac{\partial \tilde{u}_2}{} + t_3 . \frac{\partial u_3}{\partial x} \qquad (2.31)$$

Intogration of equation 2.31 across the membrane gives the well known expression for the diffusion potential. A full discussion of this expression and the way in which it may be used to calculate $\frac{\partial \tilde{u}_1}{\partial x}$ and $\frac{\partial \tilde{u}_2}{\partial x}$ is given in Appendix A.2.

It is now possible to calculate the diffusional flows of salt and water, namely the salt flow, J_S, and the osmotic flow, J_3.

Although the method of derivation of these equations is quite general, the final forms given here apply only to the case in which the electrolyte is of the 1:1 type.

2.2.1.4 Osmotic Flow

From a substitution of equations 2.27, 2.28 and 2.31 into equation 2.29c the expression below for osmotic flow, J_3, is obtained

$$J_3 = (\ell_{13} - \frac{t_1}{z_1} \cdot t_3\alpha).(-\frac{\partial u_1}{\partial x}) + (\ell_{23} - \frac{t_2}{z_2} \cdot t_3\alpha).(-\frac{\partial u_2}{\partial x}) + (\ell_{33} - t_3^2\alpha)(-\frac{\partial u_3}{\partial x}) \qquad (2.32)$$

For a 1:1 electrolyte it can easily be shown that

$$\ell_{13} - \frac{t_1}{z_1} t_3\alpha = \ell_{23} - \frac{t_2}{z_2} t_3\alpha \qquad (2.33)$$

The chemical potential of the salt u_{12} is made up of the sum of the chemical potentials of the two ions, i.e.

$$u_{12} = u_1 + u_2 \qquad (2.34)$$

Using equations 2.33 and 2.34, equation 2.32 becomes

$$J_3 = (\ell_{13} - \frac{t_1}{z_1} t_3\alpha)(-\frac{\partial u_{12}}{\partial x}) + (\ell_{33} - t_3^2\alpha)(-\frac{\partial u_3}{\partial x}) \qquad (2.35)$$

If J_3 is taken to be positive then $(-\frac{\partial u_3}{\partial x})$ is positive and $(-\frac{\partial u_{12}}{\partial x})$ is negative. $\ell_{33}(-\frac{\partial u_3}{\partial x})$ is positive and indicates the direct effect of a force causing a flow on water, while the negative $-t_3^2\alpha.(-\frac{\partial u_3}{\partial x})$ term represents the drag from the ions in the system via the electrical part of the force. The $(\ell_{13} - \frac{t_1}{z_1} t_3\alpha)(-\frac{\partial u_{12}}{\partial x})$ term measures the reduction in water flow caused by a coupling drag between salt and water.

2.2.1.5 Salt Flow

For a 1:1 electrolyte the salt flow J_S may be written

$$J_S = J_1 = J_2$$

therefore commencing with, say, equation 2.29a and, as in osmotic flow, substituting equations 2.27, 2.28 and 2.31 into 2.29a, the salt flow is

$$J_S = (\ell_{11} - \frac{t_1^2}{z_1^2}\alpha)(-\frac{\partial u_1}{\partial x}) + (\ell_{12} - \frac{t_1 t_2}{z_1 z_2}\alpha)(-\frac{\partial u_2}{\partial x}) + (\ell_{13} - \frac{t_1}{z_1} t_3\alpha)(-\frac{\partial u_3}{\partial x}) \qquad (2.36)$$

Again for a 1:1 electrolyte

$$\ell_{11} - \frac{t_1^2}{z_1^2}\alpha = \ell_{12} - \frac{t_1 t_2}{z_1 \cdot z_2}\alpha = (\ell_{11}\ell_{22} - \ell_{12}^2)/\alpha \qquad (2.37)$$

and using equations 2.37 and 2.34 equation 2.36 becomes

$$J_S = 1/\alpha(\ell_{11}\ell_{22} - \ell_{12}^2)(-\frac{\partial u_{12}}{\partial x}) + (\ell_{13} - \frac{t_1}{z_1} t_3\alpha)(-\frac{\partial u_3}{\partial x}) \qquad (2.38)$$

Taking J_S as positive then $(-\frac{\partial u_{12}}{\partial x})$ is positive and $(-\frac{\partial u_3}{\partial x})$ is negative. $1/\alpha(\ell_{11}\ell_{22} - \ell_{12}^2)(-\frac{\partial u_{12}}{\partial x})$ represents the flow of salt under the direct force $(-\frac{\partial u_{12}}{\partial x})$ and the $(-\frac{\partial u_3}{\partial x})$ term measures the reduction in salt flow brought about by salt-water coupling. Effectively equations 2.35 and 2.38 amount to a redefinition of the flows in the system by assuming that the mobile species are salt (s) and water. This would make the phenomenological equations

$$J_S = \ell'_{SS} X_S + \ell'_{S3} X_3$$
$$J_3 = \ell'_{3S} X_S + \ell'_{33} X_3$$

and comparison of these equations with equations 2.35 and 2.38 shows that the transformation has preserved the O.R.R.

Equations 2.24a, 2.24b, 2.26, 2.35 and 2.38 exhaust the independent experiments which can be performed under isobaric, isothermal conditions - leaving five equations with six unknown ℓ_{ij}. To obtain a solution for the ℓ_{ij} a specific ℓ coefficient assumption must be made and in section 5.1 various possible assumptions will be critically examined.

2.2.2 Frictional or R - coefficient approach

For the system studied, equation 2.6 may be written

$$X_i = \sum_{k=1}^{4} R_{ik} J_k \qquad (i=1,2,3,4) \qquad (2.39)$$

In this form the R_{ik} are frame of reference dependent, but with the additional assumption

$$\sum_{i=1}^{4} c_i R_{ik} = 0 \qquad (2.40)$$

it can easily be shown that the R_{ik} become uniquely specified (21) i.e. regardless of whether solvent fixed or membrane fixed flows are employed, the resultant R_{ik} will be the same.

Proceeding as in section 2.2.1, it can be shown that the equations obtained from the electrical experiments become

$$z_1 F^2/\bar{K} = t_1/z_1 R_{11} + t_2/z_2 R_{12} + t_3 R_{13} \qquad (2.41a)$$

$$z_2 F^2/\bar{K} = t_1/z_1 R_{21} + t_2/z_2 R_{22} + t_3 R_{23} \qquad (2.4.b)$$

$$0 = t_1/z_1 R_{31} + t_2/z_2 R_{32} + t_3 R_{33} \qquad (2.41c)$$

and from the experiments with concentration gradients, the equations become

$$X_1^c = R_{11} J_1 + R_{12} J_2 + R_{13} J_3 \qquad (2.41d)$$

$$X_2^c = R_{21} J_1 + R_{22} J_2 + R_{23} J_3 \qquad (2.41e)$$

$$X_3^c = R_{31} J_1 + R_{32} J_2 + R_{33} J_3 \qquad (2.41f)$$

Only two of equations 2.41 d-f are independent, however, because of equation 2.30 ($\frac{t_1}{z_1} X_1 + \frac{t_2}{z_2} X_2 + t_3 X_3 = 0$), and again there are five equations with six unknowns. (Or perhaps more rigorously, nine equations with ten unknowns as the R_{4K} may be calculated from equation 2.40). The frictional coefficient approach does not explicitly describe flows in terms of forces and consequently does not give simple equations for the derived flows J_S and J_3, or the conductivity, transport and transference numbers. It is therefore as well to leave them in the form given in equations 2.41a-f. The R coefficients are nevertheless extremely useful, since first of all they are frame of reference independent as discussed above, and also can be interpreted physically on a basis which parallels that of friction in a mechanical situation. In addition there is the great advantage of being able to calculate the R_{4K} which measure the frictional interaction between the mobile species and the matrix itself. This is particularly interesting in the membrane under study for the quaternary ammonium-halide interaction. In the ℓ coefficient approach, frame of reference interactions are included in the coefficients and no explicit description of an interaction with the matrix, ℓ_{i4}, is obtained. On the solvent fixed frame of reference, which is particularly useful when the solution analogy is discussed, the coefficient b_{i4} is obtained, but here frame of reference interactions with solvent are included, and hence no unambiguous measure of matrix interactions is obtained via mobility coefficients. This point will be raised again when coupling coefficients are discussed (Section 5.2.3.).

Very closely related to the R coefficient approach is that given by Spiegler (15) who explicitly uses the frictional concept in deriving his phenomenological equations. According to Spiegler, the thermodynamic driving force on a substance i in the steady state is exactly balanced by the frictional forces between i and all other species acting in the opposite direction. These frictional forces, F_{iK}, are proportional to the difference in relative velocities of species i and k and can be written

$$F_{iK} = \bar{X}_{iK}(v_i - v_K) \qquad (2.42)$$

where $\bar{X}_{iK}$ is the frictional coefficient between one mole of species i with the existing concentration of k around it in the membrane phase. The velocities of the species are taken relative to the matrix. These $\bar{X}_{iK}$ can be related simply to R_{iK} by the equations (22)

$$R_{ii} = \frac{\sum \bar{X}_{iK}}{c_i} \quad \text{where the summation is carried out over all species in the membrane.} \qquad (2.43)$$

and $$R_{iK} = R_{Ki} = -\frac{\bar{X}_{iK}}{c_K} = -\frac{\bar{X}_{Ki}}{c_i} \quad (i \neq k) \qquad (2.44)$$

Equation 2.44 demonstrates one of the less useful facets of the Spiegler approach, i.e. $\bar{X}_{iK} \neq \bar{X}_{Ki}$ and while the model is very useful conceptually, calculations of frictional coefficients have been done in terms of R_{iK} rather than $\bar{X}_{iK}$.

As attention has been drawn to the frictional analogy which plays an important part in interpretation, it is appropriate to discuss this further. The macroscopic concept of friction loses its meaning at the molecular level and the word must be taken to apply to the collisional retardation of particles by other particles.

Spiegler points out the danger of carrying the mechanical friction analogy too far but nevertheless uses it in his model, and so constrains the $\overline{X}_{ik}$ to be positive definite. This is a serious limitation as R_{ik} cross coefficients are found to be both positive and negative. The too literal interpretation of the word friction has also caused several authors (19)(23)(24) to regard the R coefficient approach with disfavour as it would involve the idea of 'negative friction'. The most generally accepted interpretation of the signs of the R coefficients has been given by Kedem (25) who considers that R coefficients between attractive species, i.e. those which tend to drag each other along, are negative, and those which measure repulsive interactions are positive.

2.2.3 Isotope Interactions

Extensive use of tracers is made in this work to measure diffusion coefficients, transport numbers, salt and electroosmotic flows, and in general the study of membrane transport processes depends considerably on the relative ease with which minute quantities of radioactive isotope can be detected. For a considerable time it was assumed that isotope - isotope interactions were negligible (15)(26) but later work (27)(28) has shown that, for water and counterions, isotope-isotope interactions can be important. The rigorous theoretical examination has been given by Kedem and Essig (29) who consider the validity of various relations which rely on the measurement of tracer fluxes, in the presence of isotope-isotope interactions.

From the point of view of this work their most important conclusion is that the relation

Net flux = Influx - Outflux

remains true whether there is isotope interaction or not.

In the following brief discussion of self diffusion (conforming to the general approach of Kedem and Essig) a frictional coefficient representation, which considers the local value of these coefficients across the membrane, is used.

A self diffusion experiment is carried out by placing a membrane between two identical solutions, adding tracer to one side and measuring its rate of appearance on the other. There are therefore no gradients of electrical potential, salt concentration or activity coefficients across the membrane and the thermodynamic forces X_i reduce to

$$X_i = \left(-\frac{\partial \tilde{u}_i}{\partial x} \right) = RT \left(-\frac{\partial \ln c_i}{\partial x} \right) = \frac{RT}{c_i} \left(-\frac{\partial c_i}{\partial x} \right) \qquad (2.45)$$

where i = 1,1' when 1 denotes the bulk ion of which 1' is a tracer. The treatment proceeds by assuming 1 and 1' are separate ionic species. Therefore, for any local region of the exchanger, the phenomenological equations are

$$X_1 = r_{11} J_1 + r_{11'} J_1' + \sum_{i=2,3} r_{1i} J_i \qquad (2.46a)$$

$$X_1' = r_{1'1} J_1 + r_{1'1'} J_1' + \sum_{i=2,3} r_{1'i} J_i \qquad (2.46b)$$

$$X_j = r_{j1} J_1 + r_{j1'} J_1' = \sum_{i=2,3} r_{ji} J_i \quad (j=2,3) \qquad (2.46c)$$

By the definition of the system, all X_i and J_i other than 1 and 1' are zero, and equations 2.46 may be written

$$X_1 = r_{11} J_1 + r_{11'} J_1' \qquad (2.47a)$$

$$X_1' = r_{1'1} J_1 + r_{1'1'} J_1' \qquad (2.47b)$$

$$0 = r_{j1} J_1 + r_{j1'} J_1' \quad (j=2,3) \qquad (2.47c)$$

The condition of zero net current imposes the further restriction

$$J_1 + J_1' = 0 \qquad (2.48)$$

With equations 2.45 and 2.48, equation 2.47a becomes

$$\frac{RT}{c_1}\left(-\frac{\partial c_1}{\partial x}\right) = (r_{11} - r_{11'})\,J_1 \qquad (2.49)$$

If equation 2.49 is solved for J_1, then comparison with the classical form of Fick's first law of diffusion (viz. $J_1 = d_{11}\left(-\frac{\partial c_1}{\partial x}\right)$) yields the relation

$$d_{11} = \frac{RT}{c_1\,(r_{11} - r_{11'})} \qquad (2.50)$$

Experimental data is obtained for the membrane as a whole, therefore equation 2.50 must be integrated across the membrane to give these average membrane values. The integrated form of equation 2.50 is

$$D_{11} = \frac{RT}{c_1\,(R_{11} - R_{11'})} = \frac{RTd}{c_1 R^X} \qquad (2.51)$$

where R^X is the exchange resistance and d is the membrane thickness. It will be obvious from equation 2.51 that if the isotope-isotope interaction term $R_{11'}$ is an appreciable fraction of the resistance to net flow R_{11} then any theory (15) which uses diffusion coefficients alone to calculate R_{11} must give wrong answers.

Using a similar method Kedem and Essig derive the expression below for the flux ratio in the presence of isotope interaction.

$$\ln(f) = \ln\left(\frac{\text{forward flow}}{\text{back flow}}\right) = \frac{JR^X}{RT} \qquad (2.52)$$

where J is the net flow and f is the flux ratio..

For any charged species i, when an electrical force is applied, the net flow of i, J_i, is given by $\frac{t_i I}{z_i F}$

Substitution of this and equation 2.51 into equation 2.52 gives

$$\ln(f) = \frac{t_i Id}{z_i D_{ii} c_i F}$$

which is the usual form of the flux ratio expression.

2.3 Nernst-Planck Equations

The overall flux J_i of any species i in an ion exchanger is composed of three terms (30) (J_i) diff. the flux caused by the chemical potential gradient, (J_i)el, the flux caused by the electrical potential gradient and (J_i) con. the flux caused by convection.

The diffusion flux (J_i) diff. is given by

$$(J_i)\ \text{diff.} = -\frac{D_{ii} c_i}{RT}\ \text{grad.}\ u_i \qquad (2.54)$$

where u_i is the chemical potential of species i.

The flux caused by electrical potential gradient (J_i) el may be written

$$(J_i)\ \text{el} = -u_i' z_i c_i \text{grad}\ \phi \qquad (2.55)$$

where u_i' is the electrochemical mobility of species i.

u_i' can be related to the diffusion coefficient of i by the Nernst-Einstein equation $u_i' = \frac{D_{ii} \cdot F}{RT}$, so that equation 2.55 may be rewritten,

$$(J_i)\ \text{el} = -D_{ii} z_i c_i \cdot \frac{F}{RT}\ \text{grad}\ \phi \qquad (2.56)$$

The flux caused by convection (J_i) con - a direct consequence of the choice of a membrane fixed frame of reference - becomes

$$(J_i)\ \text{con} = c_i \gamma \qquad (2.57)$$

where γ is the rate of motion of the centre of gravity of the pore liquid.

Combination of equations 2.54, 2.56 and 2.57 gives the total flux of i

$$J_i = - D_{ii} c_i \left(\text{grad } u_i' + z_i \frac{F}{RT} \text{grad } \phi \right) + c_i v \qquad (2.58)$$

For simplicity, only the use of the Nernst Planck equations to describe systems without chemical potential gradients will be considered.

This restriction simplifies equation 2.58 to

$$J_i = - z_i c_i D_{ii} \frac{F}{RT} \text{grad } \phi + c_i v \qquad (2.59)$$

Equation 2.59 is not rigorous and contains several implicit and explicit assumptions. The most notable of these are a) that the Nernst-Einstein relation, strictly true only for ideal solutions, can be applied to the membrane, b) that coupling between fluxes other than by electrical forces and convection may be neglected and c) convection carries all species at the same rate (i.e. no interactions with the matrix.)

In practice assumption a) does not seem to be as bad as might appear. It is suggested that this is due to the smallness of the pores preventing the formation of ionic clouds (31) as it is known that deformations of the ionic clouds by the electric field contributes to deviations from the Nernst-Einstein relation in non ideal systems. The rate of motion of the centre of gravity of the pore liquid may be expanded as

$$v = z_4 \frac{F c_4}{P_0 V_w} \text{grad } \phi = z_4 u_3' \text{grad } \phi \qquad (2.60)$$

where $u_3' = F c_4 / P_0 V_w$ is the mobility of the pore liquid, P_0 is the specific flow resistance of the exchanger, V_w is the fractional pore volume and z_4 is the signed valency on the fixed ions.

Using equations 2.59 and 2.60 the electrical current density, I, can be written

$$I = F \sum_i z_i J_i = F \sum_i \left(- z_i^2 c_i D_{ii} \frac{F}{RT} + z_4 u_3' c_i z_i \right) \text{grad } \phi \qquad (2.61)$$

where the summation is carried out over all mobile ionic species i in the membrane (i.e. i=1, 2)

The condition of overall electroneutrality in the membrane gives the further restriction

$$\sum_i c_i z_i = 0 \qquad (i=1,2,4) \qquad (2.62)$$

and therefore

$$I = F \left(\sum_{i=1,2} \left(-z_i^2 c_i D_{ii} \frac{F}{RT} \right) - z_4^2 c_4 u_3' \right) \text{grad } \phi \qquad (2.63)$$

From the current density and Ohm's law ($I = \bar{K}$ grad $(-\phi)$), the specific conductivity becomes

$$\bar{K} = F \left(\sum_{i=1,2} \left(z_i^2 c_i D_{ii} \frac{F}{RT} \right) + z_4^2 c_4 u_3' \right) \qquad (2.64)$$

and similarly the transport number, t_i, is

$$t_i = \frac{z_i J_i F}{I} \qquad (2.23)$$

$$= \frac{z_i^2 c_i D_{ii} \frac{F}{RT} - z_4 c_i z_i u_3'}{\sum_{i=1,2} \left(z_i^2 c_i D_{ii} \frac{F}{RT} \right) + z_4^2 c_4 u_3'} \qquad (2.65)$$

To evaluate any of these quantities it is essential to calculate u_3'. From its definition,

$$(J_3)_{el} = z_4 c_3 u_3' \text{grad } \phi \qquad (2.66)$$

and from equations 2.21, 2.25 and 2.26

$$(J_3)_{el} = (t_3 \bar{K}/F) \text{ grad } (-\phi) \qquad (2.67)$$

Comparison of equations 2.66 and 2.67 yields

$$u_3' = - \frac{t_3 \bar{K}}{c_3 F z_4} \qquad (2.68)$$

This identity for u_3' may now be used in equations 2.63, 2.64 and 2.65 to give

a) From equation 2.63

$$I = \left(\sum_{i=1,2} \left(- z_i^2 c_i D_{ii} \frac{F}{RT} \right) + z_4 c_4 t_3 \bar{K} / c_3 \right) \text{grad } \phi \qquad (2.69)$$

b) From equation 2.64, either

$$\bar{K} = \frac{F^2}{RT} \left(\frac{\sum z_i^2 c_i D_{ii}}{1 + \frac{z_4 c_4 t_3}{c_3}} \right) \qquad (2.70)$$

or

$$t_3 = \left(\frac{F^2}{RT\bar{K}} \left(\sum_i c_i D_{ii} z_i^2 \right) - 1 \right) \cdot \frac{c_3}{z_4 c_4} \qquad (2.71)$$

c) From equation 2.65

$$t_i = \frac{F^2}{RTK} z_i^2 c_i D_{ii} + \frac{t_3 c_i z_i}{c_3} \qquad (2.72)$$

Equations 2.70 - 2.72 may be used to predict $\bar{K}$, t_3 and t_i from experimental data.

2.4 Non Equilibrium Thermodynamics/Nernst-Planck Comparisons

As non equilibrium thermodynamics is completely rigorous in its description of membrane transport processes, expressing the Nernst-Planck equations in non equilibrium thermodynamic terms should highlight the consequences of the assumptions, both explicit and implicit, that this treatment makes.

For an electrical potential gradient only, the phenomenological equations are

$$J_1 = (z_1 \ell_{11} + z_2 \ell_{12}).F.\text{grad}\,(-\phi) \qquad (2.73a)$$

$$J_2 = (z_1 \ell_{21} + z_2 \ell_{22}).F.\text{grad}\,(-\phi) \qquad (2.73b)$$

and the analogous Nernst-Planck equations are

$$J_1 = \left(z_1 \frac{c_1 D_{11}}{RT} + \frac{c_1}{c_3} \cdot \frac{t_3 \bar{K}}{F^2}\right) F \text{ grad } (-\phi) \qquad (2.74a)$$

$$J_2 = \left(z_2 \frac{c_2 D_{22}}{RT} + \frac{c_2}{c_3} \cdot \frac{t_3 \bar{K}}{F^2}\right) F \text{ grad } (-\phi) \qquad (2.74b)$$

(It will be recalled that the equations for J_3 were used to establish the identity for u'_3. They need not therefore be considered any further). To proceed with the correlation of the two theoretical approaches it is necessary to use the results of the application of non equilibrium thermodynamics to self diffusion. In section 2.2.3 this was done using an R coefficient approach, but it is equally simple to adopt ℓ coefficients in which case the self diffusion coefficient D_{ii} of a species i may be written

$$D_{ii} = RT \left(\frac{\ell_{ii}}{c_i} - \frac{\ell_{ii'}}{c_{i'}}\right) \qquad (2.75)$$

where $\ell_{ii'}$ is the isotope-isotope mobility coefficient and $c_{i'}$ is the concentration of traced i.

For the counterion, in general $\frac{\ell_{11'}}{c_{1'}}$ is an appreciable fraction of $\frac{\ell_{11}}{c_1}$ but for the coion, as will be argued in a later section, $\frac{\ell_{22'}}{c_{2'}}$ is negligible in comparison with $\frac{\ell_{22}}{c_2}$. With this in mind equations 2.74a, 2.74b become

$$J_1 = \left(z_1 \ell_{11} + \frac{c_1}{c_3}(z_1 \ell_{13} + z_2 \ell_{23}) - \frac{z_1 c_1 \ell_{11'}}{c_{1'}}\right) F \text{ grad } (-\phi) \qquad (2.76a)$$

$$J_2 = \left(z_2\ell_{22} + \frac{c_2}{c_3}(z_1\ell_{13} + z_2\ell_{23}) - \frac{z_2c_2\ell_{22}'}{c_2'}\right).F.\text{grad}\,(-\phi) \qquad (2.76b)$$

$$\left(t_3\bar{K}/F^2 = z_1\ell_{13} + z_2\ell_{23}\right)$$

It is obvious from a comparison of equations 2.73 and 2.76 that (neglecting isotope-isotope interactions for the moment) the Nernst-Planck approach attempts to compensate for the neglect of ℓ_{12} by mixing in a weighted fraction of ℓ_{13} and ℓ_{23}. In so doing the O.R.R. are destroyed, as the correction to J_1 is much larger than the correction to J_2, $(c_1 > c_2)$, and has the same sign. In using the Nernst-Einstein relation an unwitting improvement is made to J_1 as the isotope-isotope interaction term (not recognised by the Nernst-Planck approach) acts in the opposite sense to the ℓ_{13}, ℓ_{23} term. It is not obvious however that this would restore the O.R.R. To see the effect on the experimental quantities it is convenient to consider the ionic currents z_iJ_i and restore $t_3\bar{K}/F^2$. Equations 2.76 become

$$z_1J_1 = \left(z_1^2\ell_{11} + \frac{z_1c_1}{c_3}\cdot\frac{t_3\bar{K}}{F^2} - \frac{z_1^2c_1\ell_{11}'}{c_1'}\right).F.\text{grad}\,(-\phi) \qquad (2.77a)$$

$$z_2J_2 = \left(z_2^2\ell_{22} + \frac{z_2c_2}{c_3}\cdot\frac{t_3\bar{K}}{F^2} - \frac{z_2^2c_2\ell_{22}'}{c_2'}\right)\text{F grad}\,(-\phi) \qquad (2.77b)$$

In equation 2.77a the second term is positive for an anion exchanger whereas $z_1z_2\ell_{12}$ should be negative. While the isotope term will to some degree compensate for this, 2.77a will almost certainly yield an overestimate of z_1J_1. The second term in equation 2.77b is negative in an anion exchanger as required but (in the membrane under consideration at least) again overestimates ℓ_{12} which means that z_2J_2 is then underestimated. In the equations for $\bar{K}$ and t_3 where $(z_1J_1 + z_2J_2)$ appears, the two errors will tend to cancel so that predictions of these quantities may be reasonable, but for t_1 and t_2, in view of the foregoing arguments, the predictions

are expected to be poor, with t_1 overestimated and t_2 underestimated (Indeed in this membrane t_2 was underestimated to the extent of being negative!)

It is clear therefore that the Nernst-Planck approach suffers from severe limitations and while its predictive qualities are useful, it can be a poor substitute for the rigorous approach.

CHAPTER 3

EXPERIMENTAL

3.1 Reagents

Sodium Chloride Dried AnalaR sodium chloride was used in the preparation of all solutions. Initially, AnalaR sodium chloride which had been twice recrystallised from water-ethanol mixtures was used in solutions for conductivity measurements on the membranes in the chloride form, but this refinement was found to be unnecessary in the light of the experimental results.

Sodium Iodide The best commercially available sodium iodide- "General Purpose Reagent" (guaranteed purity greater than 99%) - was used in the preparation of all solutions.

All other reagents mentioned were AnalaR grade unless otherwise specified. Solutions were made up in Grade A volumetric glassware at 25° C using distilled water from an all glass still.

3.2 Membrane Selection and Conditioning

Discs of membrane approximately 3.8 centimetres in diameter, cut from the original sheet, were allowed to swell in distilled water prior to subjecting them to several cycles of the conditioning process suggested by Helfferich (32). This consisted of alternate treatments of approximately 1 molar solutions of hydrochloric acid and sodium hydroxide with occasional equilibrations in distilled water and methanol.

Apart from putting the membranes through several ion exchange cycles, the acid and base removed any acid-or base-soluble impurities which could have accumulated in the membranes during the manufacturing process, and the equilibrations in methanol removed any monomer or uncrosslinked polymer. The membranes were never allowed to remain in the hydroxide

form for any length of time to avoid deterioration of the fixed groups by the Hofmann degradation (loss of the quaternary ammonium group by liberation of tertiary amine). After conditioning, the membranes (in the chloride form) were inspected microscopically for any flaws or physical defects. The survivors, in the leached chloride form, were then stored in distilled water until required for use.

When the membranes were being converted into a different ionic form, a minimum of four days equilibration was allowed. Simple re-equilibration with a solution of different concentration which did not involve ion exchange, was given a minimum of two days. During both of these processes the equilibrating solutions were changed frequently.

3.3 Weights and Dimensions

3.3.1 Wet Weights

The main difficulty in obtaining accurate wet weights is the extremely rapid loss of water from the membranes after the surface has been dried (about one milligram weight loss per fifteen seconds from a membrane weighing about 0.3 grams). Consequently, attempts to find the wet weights by drying the surface and placing between two previously weighed clock glasses gave erratic results. This procedure was therefore abandoned in favour of a kinetic method.

The membrane was removed from the solution with forceps and placed between sheets of filter paper. The adhering films of solution immediately saturated the filter paper in contact with the membrane making it unlikely that any significant weight loss could occur at this stage.

The forceps were dried, the membrane was transferred to a dry area of filter paper and a stopclock started. When the surface was absolutely moisture free, the membrane was placed on a previously weighed, open mesh platinum wire cradle suspended from the balance pan and readings taken every fifteen seconds for about two minutes. During this time the weight loss was observed to be linear and the true wet weight was found by extrapolation to zero time.

This method gave good reproducibility with a standard error of about ± 0.3 milligrams in a membrane weighing 0.3 grams.

3.3.2 Dry Weights

A leached membrane was placed between two clock glasses in a desiccator over phosphorus pentoxide. The desiccator was evacuated then placed for a minimum of twenty four hours in an oven maintained at 40° C, after which the dry weight was obtained.

It was observed that in the early stages of drying, the membranes, normally opaque in the chloride form and translucent in the iodide form, became completely transparent, but eventually became opaque as drying proceeded. After drying, the membranes were placed in distilled water and allowed to reswell. The wet weights were redetermined to ensure that the drying process was reversible (which it was within experimental error) before carrying on. During the remainder of the work, the membranes were not allowed to dry out again.

3.3.3. Thickness

Membrane thicknesses were determined with a micrometer screw gauge in two ways - directly, by applying the gauge to a number of areas over the membrane surface, and indirectly, by measuring the thickness of two

optically flat glass plates with and without the membrane in between. Both methods gave identical results within experimental error (±1.0%) and deviations in thickness over the surface as determined by the direct method were minimal.

3.3.4 Diameter

The membrane was placed between two glass plates which were then aligned on a sheet of graph paper on a travelling microscope.

The diameter obtained by averaging a number of measurements with different relative alignments of the membrane was taken as the true diameter.

(When measuring thicknesses and diameters of the membranes in the chloride form over a range of external concentrations of sodium chloride, it was observed that while the thickness decreased by about 3% between 0.1 and 2.0 molar, no decrease in diameter was observed - showing that the membranes are anisotropic).

3.4 Halide Content

The two obvious methods of obtaining the halide content of the membranes are by radioactive isotope distribution and direct titration of halide. Isotope distribution methods have the advantage that the membrane remains in the same ionic form with the same general physical properties and the added convenience that the membrane does not require to be back converted into the initial ionic form, but the general limitations of this method (see section 3.7) make an error of less than 1% - even under the most favourable conditions - almost impossible to achieve.

On the other hand a potentiometric titration of halide ion can be done extremely accurately, especially so using the linear titration plot method of Gran (49). Experimentally, a leached membrane (in either the chloride or iodide form), whose surface had been dried between filter papers, was placed in a 50 ml beaker and 10 ml of a solution of sodium nitrate of known concentration (usually about 0.5 molar) were added. Twenty four hours later, the membrane was transferred into a second 50 ml beaker and 10 ml of sodium nitrate again added and this procedure was repeated until all the halide had been removed from the membrane.

Two equilibrations were found to be sufficient to remove all the chloride from a leached chloride membrane, however three were required for leached iodide membranes reflecting the greater selectivity of the membrane for the iodide ion. (Chloride/iodide selectivities were studied in greater detail - see sections 3.7 and 7.2).

The titrant used was a solution of sodium nitrate and silver nitrate having the same ionic strength as the solution used for equilibrations. The fraction of silver nitrate was such that the end point of the titration occurred after about 5 ml had been added from the calibrated 10 ml grade A burette used. This burette, which had its tip finely drawn out, also had a silver electrode sealed into it with "Araldite" below the tap. The titration was carried out by first placing the tip of the previously filled burette below the surface of the solution to be titrated. This meant that the solution in the tip acted as a liquid junction and, as both the titrant and the solution to be titrated had the same ionic strength and similar compositions, diffusion from the tip and hence the liquid junction potential were minimised.

A silver electrode was placed in the solution to be titrated and both electrodes were connected to a Solartron digital voltmeter capable of reading to ± 0.25mV. The solution was stirred with a teflon-covered magnetic stirrer.

The silver nitrate solution was then run in until the end point of the titration had just been passed. (At the end point, the rate of change of potential per unit volume of titrant added is a maximum because of the very rapid changes in the silver ion concentration in this region). The magnetic stirrer was switched off after allowing time for thorough mixing of the solutions, and the potential and volume added were noted. The magnetic stirrer was restarted, another addition of silver nitrate made and the above procedure repeated. The titration was continued until about ten pairs of readings of potential and volume added had been obtained. The average temperature of the solution during the titration was calculated from readings taken at the beginning and end of the titration. The results were then processed by computer (program in appendix A.6) to evaluate the total halide present in the solution. The total halide present in the membrane, obtained by summing the halide from the successive equilibrations, was reproducible to ± 0.5%.

The stability of the potentials was improved by electrolysing a fresh surface on to the silver electrode in the burette before each day's runs. Although it is equally possible in theory to carry out the calculation on titration data obtained before the end point, in practice the silver ion concentration in the solution (controlled by the solubility product of silver chloride) is so low that the potentials are not reliable.

3.5 Radioactive Isotopes and Counting Methods

The isotopes used in this work were sodium-22, chlorine-36, iodine-131 and tritium, all of which were obtained from the Radiochemical Centre, Amersham. The sodium-22 and chlorine-36 were both obtained as aqueous sodium chloride solutions, the iodine-131 as aqueous sodium iodide and the tritium as tritiated water.

All radioactive counting was performed on a Nuclear Chicago Mark 1 Liquid Scintillation Spectrometer with automatic sample changer and printout. A dioxan based phosphor (33), miscible with aqueous samples, was used. Samples, which varied between 0.08 ml and 1.6 ml according to the magnitude of the isotopic flow, were added to 10 ml of phosphor contained in low potassium content glass counting vials.

Two separate problems arose from the nature of the samples.

The first was with precipitation of sodium chloride in the phosphor at sodium chloride concentrations of 0.5 molar and above. This was overcome by adding 0.4 ml aliquots of distilled water until the precipitate had dissolved. It was observed that although a 0.4 ml addition of 0.5 molar sodium chloride caused precipitation, a 1.2 ml addition did not. In general it was found that the larger the sample added, the smaller the amount of distilled water required.

The second problem was with oxidation of sodium iodide in the phosphor to form iodine. This changed the colour of the phosphor from the usual fluorescent bluish-purple to a deep yellow brown which, in turn, caused severe colour quenching. It was estimated that 90% of tritium counts and 50% of the sodium - 22 counts were lost through this quenching.

The problem was overcome by allowing the samples to stand for a day then adding sufficient of a dilute sodium thiosulphate solution to reduce the iodine and restore the phosphor to its original colour. (If sodium thiosulphate was added immediately, it was found that after a few hours the samples once more turned pale yellow).

Gamma emitters such as sodium-22 caused a peculiar effect when counting in the liquid scintillation spectrometer. If a vial counting at a high rate was preceded or followed by relatively inactive vials it was found that the backgrounds were increased in these adjacent vials. This effect was observable up to three vials away from the active one and was enough to double the background in the immediately adjacent vial. As counts of this order were being obtained in transport number runs, the effect seriously interfered with the results. It was thought that the gamma emission from the active vial was causing phosphorescence in the others but the effect was not investigated any further, being simply overcome by placing three blank vials between the high and low activity samples. Most samples were counted for twenty minutes, but the very low activity samples were counted for forty to reduce the statistical counting errors. Counting reproducibility was generally in the range $\pm$ 1-2% but tritium, with its low energy beta emission (18keV) was counted with a lower efficiency and the counting reproducibility deteriorated to about $\pm$ 3%.

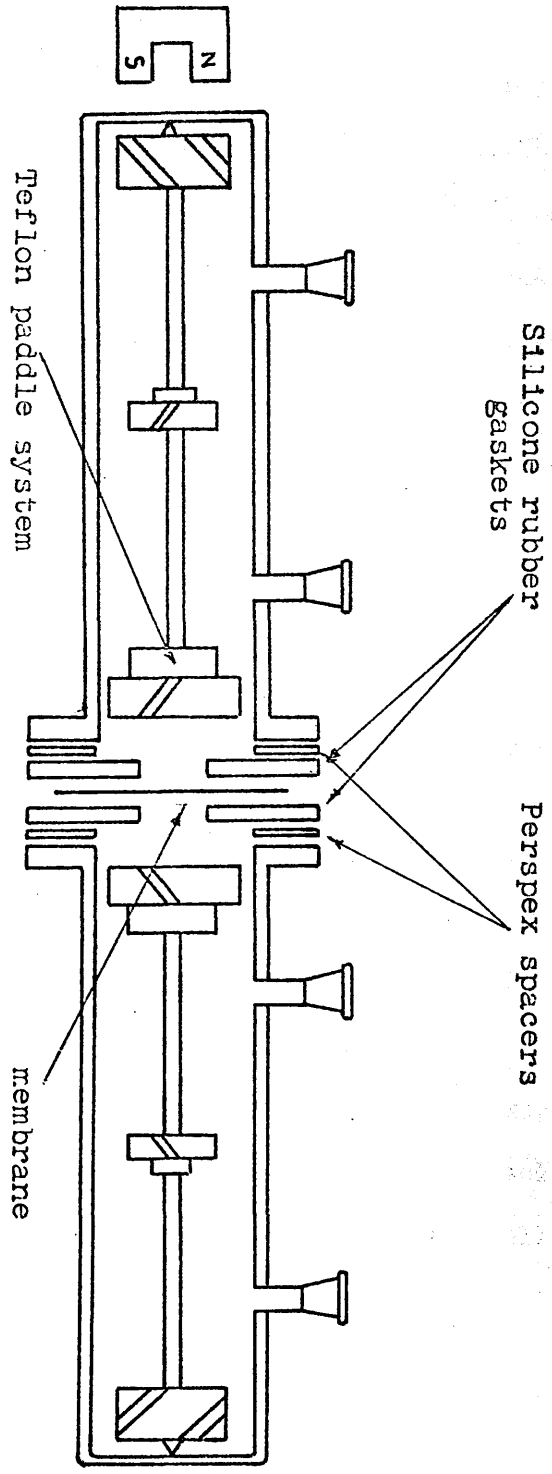


Fig. 3.1 Membrane Diffusion Cell

3.6 Tracer Diffusion

The diffusion cell was similar to that used by Mackay and Meares (34) and is represented diagrammatically in figure 3.1. The paddle system was constructed from teflon with a small magnet sealed with "Araldite" into the rear paddle in each half cell. These magnets were driven by master magnets connected to an electric motor by a gear wheel transmission system. A voltage stabiliser was used to offset voltage fluctuations in the mains supply to the electric motor in order to prevent variations in the stirring speed during the course of an experiment. Stirring speeds were measured with a Dawe 1200E stroboscope.
(This method however is not quite as straightforward as it may appear, as the paddles not only appear stationary at the true stirring speed but also at numerous harmonics. Only the true stirring speed gave sharply defined edges to the paddle blades; a harmonic gave "blurred" edges owing to the minor differences between blades).
The volume of each half cell was in the range 60-70 ml.
The membrane was mounted in the cell between two identical perspex spacers which were provided with locating pins to ensure exact coincidence such that the same area of membrane was exposed to the solutions on either side. Solutions were added simultaneously to each half cell from two grade A burettes.
The cell assembly was carried out as quickly as possible to minimise the water loss from the membrane (cf. section 3.3.1), nonetheless on dismantling the cell after a run, the membrane was invariably found to have buckled very slightly as a result of reswelling when the solutions were run in. Great care was taken to ensure that no air bubbles remained near the membrane after the cells had been filled.

It was found to be advantageous to degas the solutions under vacuum for a few minutes before adding to the half cells to prevent the subsequent formation of air bubbles on the teflon surfaces. The exposed edges of the central "sandwich" of spacers and membrane were covered with a layer of paraffin wax which sealed the membrane from the water bath in which the cell was immersed up to the sample ports. The cell was then allowed to equilibrate overnight in this bath (maintained at $25 \pm 0.1^{\circ}C$) before a run. The run was started by adding a suitable quantity of the appropriate radiotracer ion to one side of the cell.

(In general, the volume required was so small (about 0.08 ml) that the solutions supplied from the Radiochemical Centre were used without further treatment).

The stirrers were switched on, then, after allowing about five seconds for mixing, a stopclock started. When a steady state had been established, two samples were withdrawn from the active side, then samples taken from the inactive side at suitable time intervals. All samples were taken with Hamilton microlitre syringes which, when fitted with Chaney adaptors, delivered volumes reproducible to 0.1%. 0.08 ml samples were taken from the active side, but the sample size from the inactive side was varied according to the magnitude of the isotopic flow, as previously mentioned in section 3.5. Inactive solution was added to the active side vials to bring them up to the same volume as the inactive vials. This was done to ensure identical counting efficiencies in both active and inactive vials. Failure to do this resulted in serious counting errors.

When a sample had been removed from the inactive side, it was replaced by the same volume of inactive solution. A correction for this procedure was derived (Appendix A.3) and incorporated in the computer program (Appendix A.6) used to calculate the diffusion coefficient from the results.

A stirring speed of 550 r.p.m. was used for most runs. From theoretical considerations it is preferable to study diffusion in the steady state and this was done in all cases. However,in the iodide form, which has a low self diffusion coefficient and a high concentration of iodide, there was a considerable delay of up to 150 minutes before the steady state was achieved. Data collected during this time was treated by the non steady state method of Meares (35).

(Program in Appendix A.6)

Steady state results were calculated using the equation (36)

$$\bar{D}_{\beta} = \frac{dc''}{dt} \cdot \frac{V''.c.d}{c'.\bar{c}.q} \qquad (3.1)$$

This was obtained from the equation for isotopic flux in the steady state

$$J = \bar{D}_{\beta}.\bar{c}'/d \qquad (3.2)$$

including the condition for mass balance

$$q.J = V''.\, dc''/dt \qquad (3.3)$$

and the conditions for no interfacial resistance

$$\bar{c}'/\bar{c} = c'/c \text{ and } \bar{c}''/\bar{c} = c''/c. \qquad (3.4)$$

The indices ' and " refer to the active and inactive sides respectively.

$\bar{D}_A$ is the effective self diffusion coefficient in the membrane phase ($cm^2 sec^{-1}$)

J is the isotopic flux (moles $cm^{-2} sec^{-1}$)

$\bar{c}'$ is the membrane tracer concentration on the active side

d is the membrane thickness (cm)

q is the membrane area (cm^2)

dc''/dt is the rate of increase in activity on the inactive side

V'' is the solution volume on the inactive side (cm^3)

c is the bulk concentration of the traced ion in the external solution (moles cm^{-3})

and $\bar{c}$ is the bulk concentration of the same ion in the membrane (moles cm^{-3})

The above equations define the apparent diffusion coefficient $\bar{D}_A$ and take no account of the unstirred films at the solution - membrane interfaces. The thickness of these films as a function of stirring speed was obtained by the method of Scattergood and Lightfoot (28) and the true diffusion coefficient $\bar{D}$ calculated as in Appendix A.4.

It was found that only counterion self diffusion coefficients in the chloride form were corrected to any significant degree. (In the least favourable case, 0.1MNaCl, this correction amounted to 3% at 550 r.p.m.)

The membranes were also tested for asymmetry potential by measuring the potential between two silver halide electrodes, one in each half cell, before commencing the first of a series of diffusion runs. No membrane asymmetry potential could be detected within the limits of the voltmeter employed ($\pm$ 0.01mV).

The total error in the self diffusion coefficients was not greater than ± 2% except for tritium where the reduced efficiency of counting increased this to ± 3%.

3.7 Coion Uptake and Selectivity Measurements

Isotope distribution methods were used for both coion uptake and chloride/iodide selectivity measurements.

The membrane was placed in its equilibrium solution which was traced with the desired radioisotopic species and allowed to equilibrate for twenty four hours. In this process an isotopic redistribution occurred.

The membrane was then removed from this solution with forceps and blotted between filter papers . Even after this procedure, external solution still adheres to the surface of the membrane, so that simply to equilibrate the membrane in inactive solution at this stage would give an overestimate of the tracer in the membrane (37). While this would be unimportant where there is a large amount of tracer ion in the membrane and consequently any surface electrolyte would only contribute minutely, coion uptake determinations, especially at low external concentrations of electrolyte, would be seriously affected by this error.

Therefore a new set of forceps was taken and the membrane was dipped into either an inactive solution of the same concentration as the radioactive solution (coion uptake) or distilled water (selectivity procedures).

In coion uptake experiments a five second dip was allowed which was considered sufficient to dislodge the adhering film without causing significant removal of isotope from the membrane phase.

The situation is much more favourable in selectivity measurements where, as the counterions are being determined, a dip in distilled water will remove the adherent films without displacing any counterions from the membrane. (It will of course remove those counterions of the electrolyte uptake but, as the overall ionic strength in chloride/iodide selectivity measurements was 0.1 molar, coion uptake is minute).

In selectivity measurements, therefore, the membrane was dipped in distilled water for thirty seconds.

With the adhering films removed, the membrane was again blotted then placed in a 50 ml beaker. A volume of inactive solution, usually 5 ml for uptake and 10 ml for selectivity measurements, was pipetted into the beaker which was then covered with "Parafilm". After a further twenty four hours equilibration, triplicate samples were withdrawn from both radioactive solutions and counted as in section 3.5. The membrane was replaced in the active solution and the whole procedure repeated.

The method of calculation employed is set out in Appendix A.5.

Errors in the selectivity measurements were in the range 1 - 2%.

For coion uptake, errors depended very much on the concentration of the equilibrating solutions. At 0.1 molar (sodium chloride and sodium iodide) the error was no better than 10% falling to about 4 - 5% at 2.0 molar.

3.8 Membrane Conductivity

A good semipermeable membrane will by definition exclude coions efficiently. High membrane capacity favours coion exclusion and hence most commercial ion exchangers have high capacities. However a high concentration of counterions in the membrane phase leads to a high electrical conductivity and therefore presents a problem in measurement.

Many workers (34)(38)(39)(40)(41)
have employed what is known as the direct method which involves measuring the resistance between two electrodes in direct contact with a length of membrane. Although the obvious disadvantage of unknown interfacial resistances can to some degree be overcome by taking measurements at different electrode distances and subtracting, more seriously the measurements take place along the length whereas all other properties are measured normal to the membrane surface. If the membrane is in any way anisotropic then a different value of conductivity will result. The method used in this work is an indirect one (28)(42)(43) in which the total resistance of a cell containing solution and membrane is determined with and without the membrane in place. The interfacial resistance problems are eliminated by this technique but to obtain a high contribution from the membrane to the total cell resistance only small areas of membrane can be exposed and these may or may not be representative of the membrane as a whole (e.g. variations of 300% in resistance have been found (44) over the same membrane sheet).

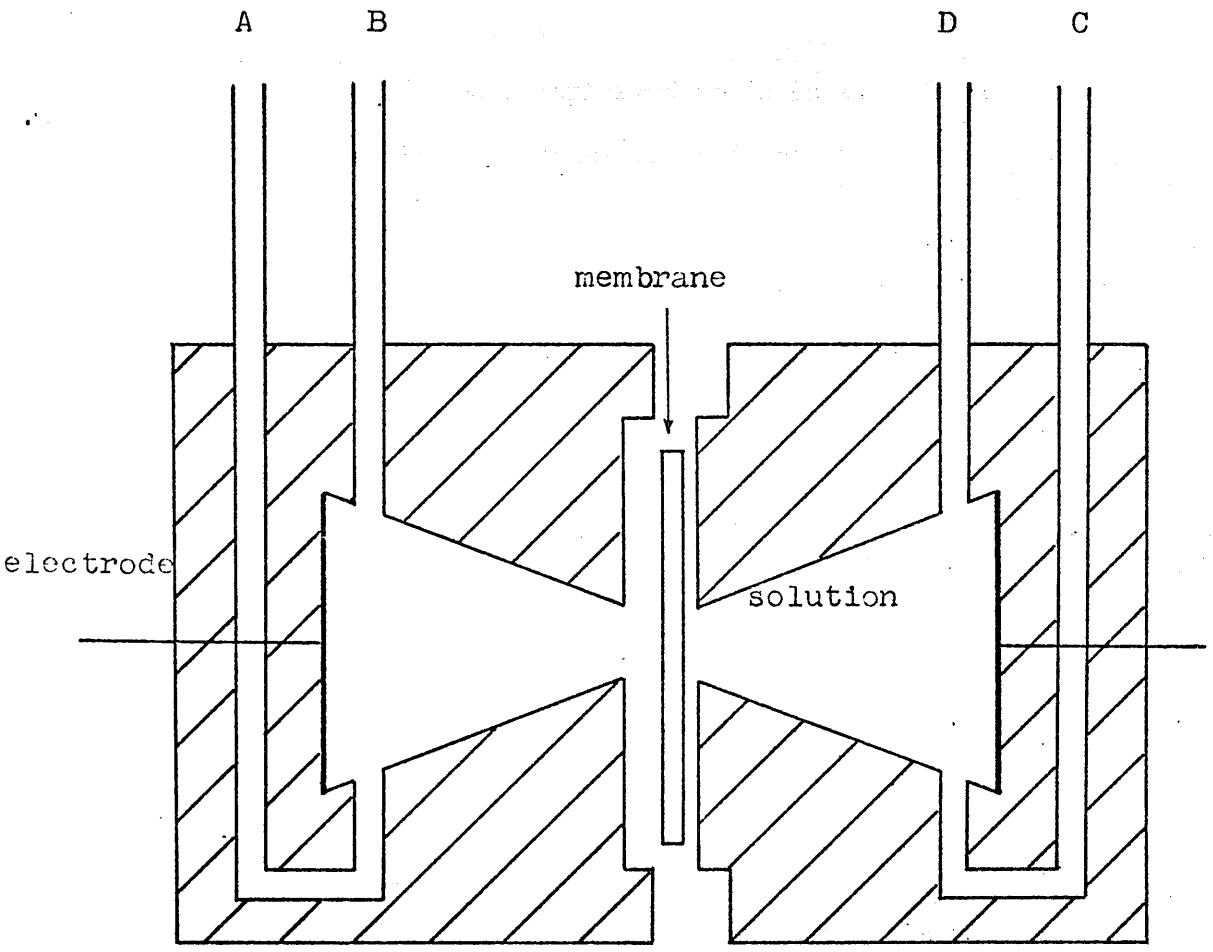


Fig. 3.2 Membrane Conductivity Cell

The cell used in this work (shown in figure 3.2)is that described in the U.S. Manual for Testing Permselective Membranes (45) and is so constructed that the volume of the solution in the cell is the same whether a membrane is present or not. Under experimental conditions, outlets B and C were connected with polythene tubing, solution entered at A and flowed to waste from D.

Conductivity measurements were performed as follows. The cell was assembled, placed inside a polythene bag and positioned in an oil bath maintained at 25 ± 0.005°C. Outlet A was connected with polythene tubing to a thermally equilibrated reservoir of the appropriate solution also present in the tank and outlet D to waste. Solution was then pumped from the reservoir into the cell and allowed to flow freely through the cell for some time to hasten thermal equilibrium. (Care was taken at this stage to ensure that no air bubbles remained in the cell. If any were observed it was usually possible to dislodge them by sharply increasing the flow for a short time.) The flow was then stopped and conductibity readings taken every ten minutes until a steady reading was obtained after which flow was restarted and the procedure repeated. Conductivity measurements were made with a Wayne Kerr B331 conductivity bridge with a manufacturer's specified accuracy of ± 0.01%.

The cell was then dismantled, a membrane placed in between the two half cells and the whole reassembled. Conductivity was again measured as above and the resistance of about 0.1 cm^2 of membrane (the area exposed in the cell) calculated by difference.

To test whether this 0.1 cm^2 was representative of the membrane as a whole, the conductivities of five membranes in equilibrium with 0.1 molar sodium chloride were determined. Four of these gave identical resistances within experimental error (±1%) and the fifth, which gave a high value of resistance, was discarded.

The conductivity of membranes equilibrated with 0.1 and 1.0 molar sodium chloride and 0.1 molar sodium iodide solutions were measured. The overall reproducibility of these measurements was ±1%.

As the total area of the membrane is many times that exposed during measurement, conduction paths other than those normal to the exposed area were considered. A theoretical treatment of these edge effects given by Barrer (46) was used to correct the measured resistances.

The effect of this correction was to lower the specific conductivity by some 4%.

3.9 Transport Numbers

Since the electrolyte uptake in these membranes is very low, counterion transport numbers may be expected to be very close to unity, but coion transport numbers must be determined. The absolute magnitude of these flows in an electrical experiment which avoids polarization must be small and therefore the standard Hittorf method employed by many workers (47) is impractical. Equally the membrane potential method (47) using electrodes reversible to counterion must yield cell potentials which are undistinguishably close to zero. Under these circumstances the net flow of radiotracer was obtained from the difference between coion tracer flows with and against the electric current. The net flow of tracer per unit area was converted

into the bulk flow of coion, J_2 from which the coion transport number t_2, may be determined (Equation 3.5)

$$t_2 = \frac{z_1 F J_2}{I} \qquad (3.5)$$

The cell used was similar to that used in diffusion measurements but with circular wide mesh platinum electrodes in each half cell about 3 cm from the membrane and parallel to it. These electrodes were electrolytically plated with silver metal from a plating solution of silver nitrate and dilute nitric acid. (The nitric acid promoted a more even deposit of silver on the platinum surfaces than was found when silver nitrate alone was used.) One of the electrodes was then almost entirely converted to silver chloride by anodising in an approximately 0.1 molar solution of hydrochloric acid, while the other was given a very light coating by the same method. Since the silver chloride tended to flake off rather easily from the heavily coated electrode, there was a practical limit to the number of coulombs which might be passed in this cell system. (The electrodes could be run at about 30 milliamps for 60 minutes). The sampling techniques and corrections used in transport numbers were the same as in the diffusion experiments. The flows of tracer both with and against the electric current were determined in the same experiment which ensured that both flows were measured under identical experimental conditions.

Sodium-22 tracer was added to the cathode compartment, stirring started, the current switched on and the experiment then conducted as a standard diffusion run until virtually all the chloride had been transferred from the cathode to the anode. The current was then reversed and the flow of tracer with the current obtained similarly.

During a run the current was monitored by measuring the potential drop across a standard resistance using a digital voltmeter. Current densities of around 4 milliamp/cm^2 were used since electroosmosis experiments had shown that polarization was not detectable at this order of current density.

Applying the same technique to coion transport number for iodide at an external concentration of 0.1 molar sodium iodide gave rather anomalous results (section 4.). This system was therefore investigated using the membrane potential method. The membrane was placed in the diffusion cell as described in section 3.6 with 0.15 molar sodium iodide in one half cell and 0.05 molar in the other. After allowing sufficient time for a steady state to be set up, measurements of the potential developed between two silver/silver iodide electrodes, (48) one in each half cell, were made.

The potential of the concentration cell is related to the average transport number across the membrane by the well known equation

$$E = RT/F \left(2t_2 \ln \frac{a_{\pm}''}{a_{\pm}'} + t_3 \ln \frac{a_3''}{a_3'} \right) \qquad (3.6)$$

(See also Appendix A.2)

These experiments proved inconclusive since the potential measured was 0 ± 0.01 mV which was the detection limit of the voltmeter used.

The uncertainty in coion transport numbers as determined by the net flow of tracer was about 10 - 12% at an external concentration of 0.1 molar sodium chloride, falling to about 5 - 7% at 2.0 molar.

3.10 Electroosmosis

The electroosmotic flow was measured by observing the volume changes in each half cell during the passage of an electric current through the membrane. Each half cell of the transport number cell was fitted with a right angled capillary such that the calibrated stem was horizontal in use. The cell was assembled in the manner described in section 3.6 except that each half cell was completely filled with degassed solution. To prevent leakage from the B.10 sockets of the half cells, all contact surfaces were covered with a very thin film of silicon grease and provided with B.10 teflon sleeves.

The solutions were stirred for several hours to absorb any air bubbles which could not be removed in the filling process. The cell assembly was then immersed up to the sample ports in a thermostat maintained at 25 $\pm$ 0.01°C and allowed to equilibrate overnight.

Once the capillary readings were steady(i.e. no leaking), the current was switched on and readings taken from both capillaries at suitable time intervals. The experiment was then repeated with the current flowing in the reverse direction. From the total volume flow in the capillary, the net flow of water, J_3, was calculated and this is related to the water transference number t_3 by equation 2.25,

viz. $t_3 = J_3F/I$.

To determine the effect of current density, measurements were made at 1 and 4 milliamp/cm^2 for 0.5, 1.0 and 2.0 molar sodium chloride. In addition at 0.1 molar sodium chloride a current density of 9 milliamp/cm^2 was used since at this concentration the membrane would be most susceptible to polarization.

The effect of stirring speed was determined in the range 250 - 550 r.p.m. and found to be negligible.

Similar experiments with the membrane equilibrated with 0.1 molar sodium iodide were unsuccessful owing to movement of the membrane in the electric field - a direct consequence of the much higher resistance in this form. Within the time limits imposed by the electrodes, linear plots were never obtained and this method had to be abandoned. The water transference number was obtained by determining the net flow of tritiated water by the method described for coion transport numbers.

Transference numbers obtained by the capillary method were reproducible to ± 1.5% but with tracer experiments only to ± 10%.

3.11 Osmosis

Osmotic experiments were made using exactly the methods described for electroosmotic flow except that the solutions on either side of the membrane differed in concentration. The assembled cell was left overnight to establish a steady state of diffusion and osmosis and refilled with fresh solutions before beginning the osmosis experiment. Capillary readings were then monitored with time as before. The time scale for these experiments ranged from a day or less for sodium chloride to some ten days for sodium iodide experiments where the osmotic flow of water was exceptionally small.

Osmotic flows were determined with 0.15/0.05 molal and 1.5/0.5 molal sodium chloride and 0.15/0.05 molal sodium iodide concentration gradients. The overall reproducibility of osmotic flows as determined by these methods was ± 3% in any given experiment.

3.12 Salt Flow

Salt flow was measured by determining the flow of coion tracer with and against the salt concentration gradient across the membrane. It was not possible to measure both flows in one run as was done in transport number experiments but against this there was no restriction on the time which could be taken, and thus both forward and back flows could be obtained with an accuracy similar to self diffusion flows.

Once again the experiment was set up with a salt concentration gradient overnight in order to allow a steady state to be established across the membrane and solutions were replaced before commencing an experiment. The technique was once more identical to that used in self diffusion experiments.

Salt flows across the membrane were determined with 0.15/0.05 and 1.5/0.5 molal sodium chloride concentration gradients and the reproducibility of these experiments was $\pm$ 3 - 4%.

CHAPTER 4

RESULTS AND DISCUSSION OF INDIVIDUAL EXPERIMENTS

4.1 General Physical Characteristics

The general physical characteristics of the AMF A-104 anion exchange membranes used in this study are set out in Table 4.1. It will be observed that there is very good agreement of the ion exchange capacities of the three membranes. A wide choice of units in which to express the capacity is possible (50) but they all have the disadvantage that the same membrane in a different ionic form will give a different value - a situation which is unsatisfactory. Direct comparison is allowed by the units used here which are independent of both ionic form and water content. There has been little work done on AMF A-104 membranes as such and only two studies are useful. Christensen (51) expresses his capacities as meq./ml of the membrane and with an external concentration of 0.1 molar in sodium chloride obtains a value of 1.048, which is in excellent agreement with this work. (1.030). On the other hand Crabtree and Glueckauf (52) obtain a value of 1.205 for the capacity expressed in meq./g. wet which is in rather poor agreement (1.050). Further inspection of Crabtree and Glueckauf's data reveals that their membranes have a considerably lower water content (0.11 as against 0.17 on a g/g wet basis). The American Machine and Foundry Company's own specification is 20% on a g/g dry basis in the chloride form. The value from this work is 20.2%.

TABLE 4.1

GENERAL PHYSICAL CHARACTERISTICS OF A.M.F. A-104 MEMBRANES

Ionic Form	MEMBRANE 11 Chloride		MEMBRANE 4 Chloride		MEMBRANE 10 Iodide
Dry Wt. (g)	0.2257		0.2264		0.2437
Halide content (meq)	0.2848		0.2857		0.2752
Wt. Matrix (g)	0.2156		0.2163		0.2088
Capacity (meq/g matrix)	1.321		1.320		1.318
External Soln	0.1MNaCl	0.5MNaCl	1.0MNaCl	2.0MNaCl	0.1MNaI
Wet Wt. (g)	0.2714	0.2686	0.2662	0.2639	0.2631
Radius (cm)	1.936	1.940	1.940	1.940	1.870
Thickness (cm)	0.0235	0.0230	0.0228	0.0227	0.0220
Volume (cm^3)	0.2767	0.2721	0.2697	0.2685	0.2418
Wt. Water (g)	0.0457	0.0421	0.0394	0.0366	0.0194
Uptake (meq)	4.07×10^{-4}	3.558×10^{-3}	1.089×10^{-2}	2.523×10^{-2}	2.26×10^{-4}
c_1 (meq/ml. mem)	1.030	1.063	1.100	1.158	1.139
c_2 (meq/ml. mem)	1.471×10^{-3}	1.308×10^{-2}	4.036×10^{-2}	9.395×10^{-2}	9.34×10^{-4}
c_3 (meq/ml. mem)	9.180	8.596	8.116	7.573	4.457
c_4 (meq/ml. mem)	1.029	1.050	1.059	1.064	1.138

A striking feature of Table 4.1 is the massive drop in water content when the counterion is changed from chloride to iodide with the external solution concentration maintained at 0.1 molar. The magnitude of the change is much larger than would be expected on the basis of different hydrated ionic sizes and the implications of the observation will be discussed in Section 4.2.4.

As the external sodium chloride solution concentration is increased from 0.1 to 2.0 molar, the wet weight, water content and thickness decrease while coion uptake increases as might be expected from general theory. The exception is the radius which remains constant, showing that the membranes are anisotropic. Anisotropy has previously been observed with two other AMF cation exchange membranes, AMF C-103 (53) (the cation exchange analogue of AMF A-104) and AMF C-60 (54), which suggests that this is a consequence of the manufacturing process.

There appears to be no obvious explanation for the transparency of the membranes observed in the early stages of drying, although similar behaviour by AMF C-60 and ACI cation exchange membranes has been reported (38).

In the remainder of this work, no distinction will be made between membranes 4,10 and 11 as results from several transport experiments conducted on all three membranes in equilibrium with 0.1 molar sodium chloride gave identical results within the limits of experimental error.

4.2 Self Diffusion

For all the systems studied, the self diffusion coefficients of counterion, coion and water were measured. A true comparison of diffusion coefficients may be made only after they are corrected for the effects of film diffusion at the membrane solution interfaces and path tortuosity within the membrane. In counterion diffusion both effects are usually important but for coion and water the unstirred films tend to become less important as rate determining steps (See Appendix A.4) and can often be ignored. As tortuosity corrections are very important for all mobile species, the discussions of diffusion results will be opened with a section on this topic.

4.2.1 Tortuosity

A mobile species diffusing from one side of a membrane to the other is forced to take a path longer than the free solution path owing to the obstruction of the polymer segments. In the absence of any interactions with the matrix other than simple obstruction, the measured diffusion coefficient of the mobile species, $\bar{D}$, (previously corrected for the effects of film diffusion) in the membrane should be related to that in a solution of the same concentration, Do, by a purely geometrical tortuosity factor. Attempts have been made to estimate this factor, notably by Wheeler, (55), Mackie and Meares (56) and Prager (57).

Wheeler's relation,

$$Do = \bar{D} . \bar{v}_w^{2} \qquad (4.1)$$

where v_w is the volume fraction of the pore liquid, is intrinsically unsatisfactory as it tends to the value 2.0 instead of 1.0 as v_w tends to unity. On the other hand Mackie and Meares' relation

$$Do = \bar{D}.\left(\frac{2}{v_w} - 1\right)^2 \qquad (4.2)$$

does tend to the correct limits and has been widely tested in the literature. The relation gives a good correlation between membrane diffusion coefficients of counterions, coions and water in Zeo karb 315 phenol sulphonic acid membranes and their values in aqueous solutions of the same concentration (58) but other workers with other membrane systems have found poor agreement (38)(52)(54)(59)(60)(61). The overall tendency displayed in these results suggests that equation 4.2 overcorrects, this being particularly so in membranes with low values of v_w. The reason for this behaviour is not difficult to ascertain as the model employed suffers from several oversimplifications, particularly the assumption that all the tortuous paths have the same length. In practice there must be a distribution of tortuous path lengths and in a membrane with a low value of v_w especially, those shorter than average will contribute disproportionately to the total flux. The application of equation 4.2 to the membrane diffusion coefficients in these circumstances must lead to an overcorrection. An expression derived from a more general model has been given by Prager (57) viz.

$$Do = \frac{\bar{D}x\ (2 - 2v_w + 2v_w \ln v_w - 0.5\ (\ln v_w)^2.\ v_w)}{(1 - v_w + v_w \ln v_w)\ x\ v_w} \qquad (4.3)$$

On rearranging equation 4.3

$$Do = \bar{D}\ x\ \left(\frac{2}{v_w} - \frac{0.5\ (\ln v_w)^2}{(1 - v_w + v_w \ln v_w)}\right) \qquad (4.4)$$

and using the first term of a series expansion for $\ln v_w$; $\frac{2(v_w - 1)}{v_w + 1}$,

which is valid when v_w is close to unity, the relationship becomes

$$Do = \bar{D}\left(\frac{2}{v_w} - \frac{2}{1 + v_w}\right) \qquad (4.5)$$

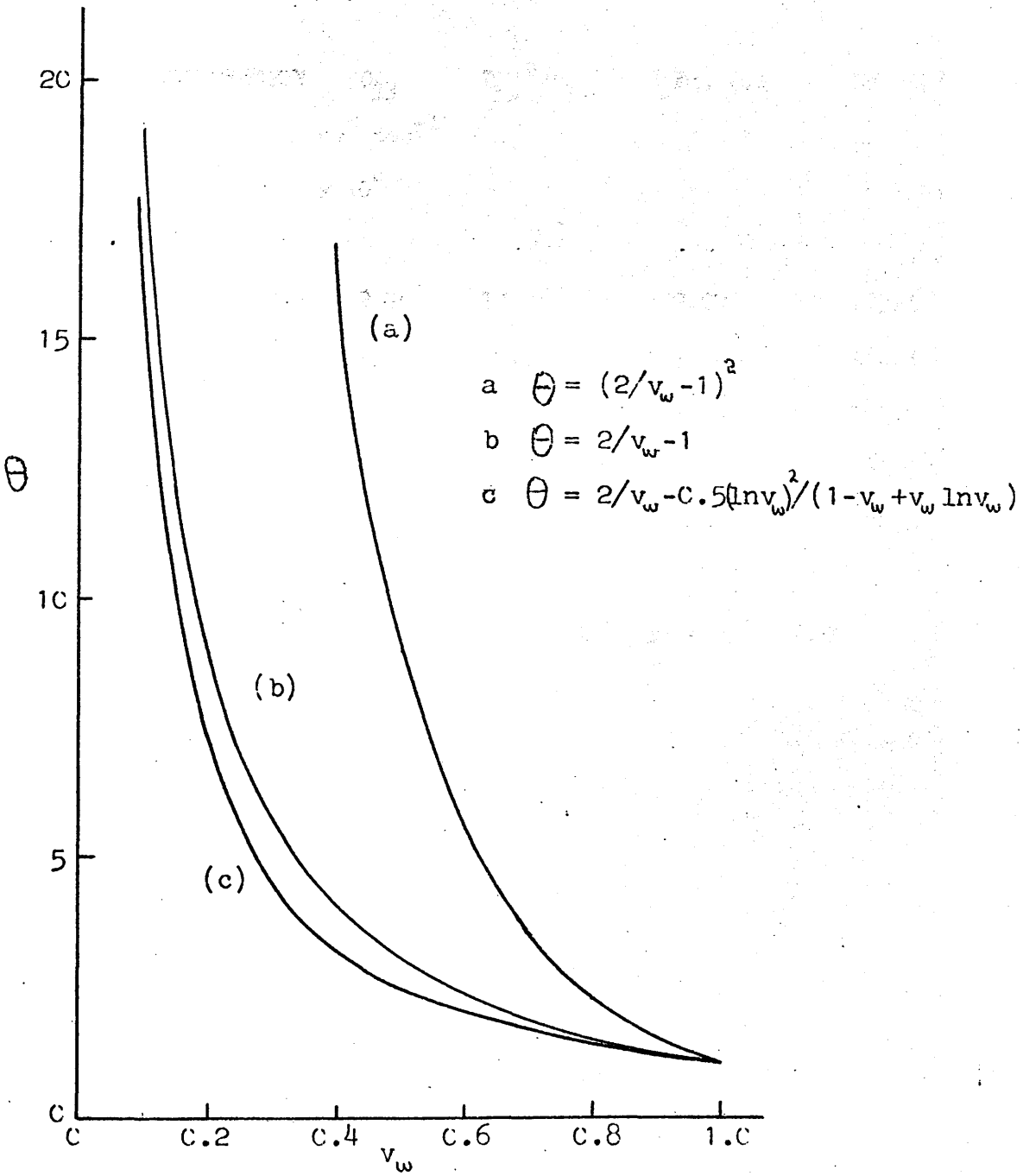


Fig. 4.1 Tortuosity Expressions

TABLE 4.2

WATER SELF DIFFUSION RESULTS AND TORTUOSITY FACTORS

EXTERNAL CONCENTRATION	D_{33} $cm^2\ sec^{-1}$ $\times 10^6$	D_{33}^{o}/D_{33}	Eq. 4.4	Eq. 4.2
0.1 M NaCl	2.36	10.34	9.09	123.4
0.5 M NaCl	1.93	12.64	9.80	142.3
1.0 M NaCl	1.61	15.16	10.46	161.0
2.0 M NaCl	1.56	15.64	11.32	186.9
0.1 M NaI	0.843	28.94	20.57	572.6

$$D_{33}^{o} = 2.44 \times 10^{-5}\ cm^2 sec^{-1} \quad (62)$$

In this form the similarities and differences of equations 4.2 and 4.5 are more obvious. Figure 4.1 shows a plot of $\frac{2}{v_w} - \frac{0.5\,(\ln v_w)^2}{1 - v_w + v_w \ln v_w}$, $\left(\frac{2}{v_w} - 1\right)^2$ and $\frac{2}{v_w} - 1$ over the range $0 \leqslant v_w \leqslant 1$. The experimental determination of tortuosity factors would appear to be quite straight forward, merely involving the measurement of Do and $\bar{D}$ for a suitable species. The problem however is to find a species which does not interact appreciably with the matrix. Ionic species thus cannot be utilised, as counterions interact strongly with the fixed ions, and coions interact with the counterions. The diffusion of small uncharged organic molecules such as urea, ethanol, glycol, offers a superficially attractive method of determining the tortuosity, but there are complications caused by adsorption of the organic molecules on to the organic polymer chains (58). The mobile species which seems to satisfy the conditions best is water. The marked structuring of liquid water and its high concentration inside the membrane will tend to make water-water interactions of prime importance. Diffusion of water through the membrane should thus be little affected by anything other than path tortuosity (although this may not be so in phenol sulphonic acid type membranes where the - OH group could interact appreciably) and so appears to offer the best available experimental test of the tortuosity models.

4.2.2. Water Diffusion

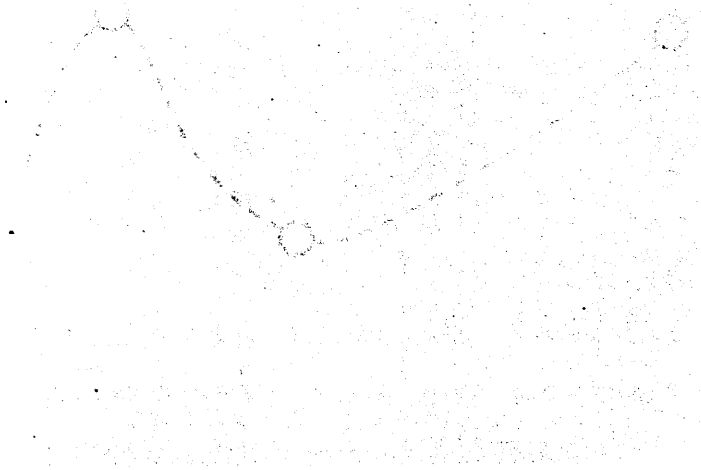
The results of self diffusion experiments using tritiated water are shown in Table 4.2. Values of D_{33}^{o}/D_{33} in the same table were calculated on the assumption that the water inside the membrane behaves little differently from water in the pure liquid. D_{33}^{o} was therefore taken as the self diffusion coefficient of tritiated water in pure

TABLE 4.3

COION SELF DIFFUSION RESULTS

EXTERNAL CONCENTRATION	D_{22} ($cm^2 sec^{-1}$) x 10^7	$D_{22}.\theta$ ($cm^2 sec^{-1}$) x 10^6
0.1 M NaCl	2.18	2.25
0.5 M NaCl	2.74	3.46
1.0 M NaCl	2.44	3.70
2.0 M NaCl	2.71	4.24
0.1 M NaI	0.091	0.263

$$\theta \equiv D_{33}^{\circ}/D_{33}$$



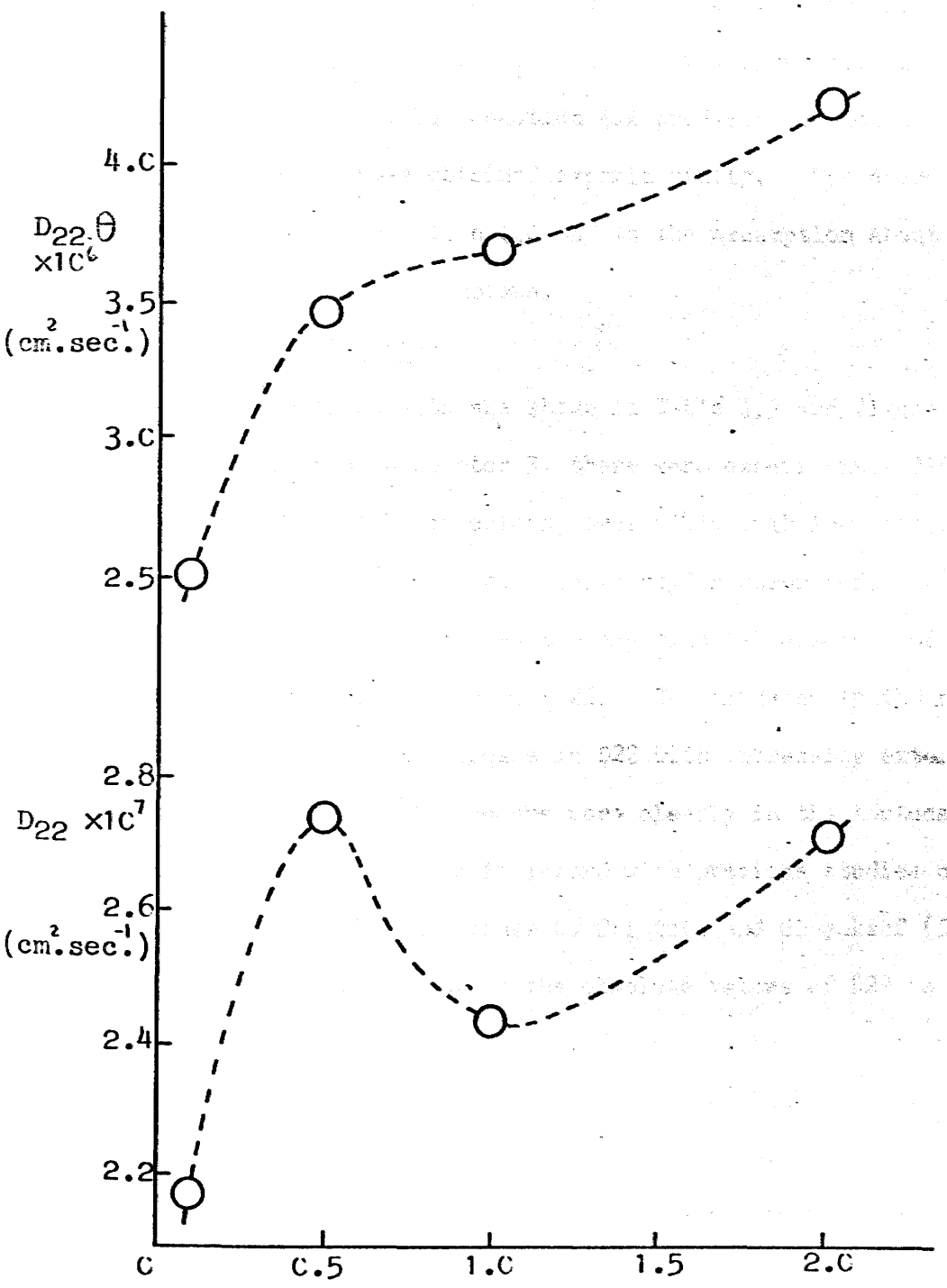


Fig. 4.2 Coion Self Diffusion Coefficients

water, 2.44×10^{-5} (62). The results in Table 4.2 also show that equation 4.2 grossly overcorrects, which is not surprising in the light of comments above, but equation 4.4 predicts tortuosity factors reasonably close to those obtained experimentally. The evidence lends support both to equation 4.4 and to the assumption about behaviour of water in the membrane.

4.2.3 Coion Self Diffusion

Coion self diffusion results are shown in Table 4.3 and figure 4.2. As has been mentioned in Chapter 3, there were experimental difficulties in determining the uptake of coions, especially with low external salt concentration. As a result the uncertainty in coion diffusion coefficients is much greater than the experimental accuracy of diffusion fluxes which were reproducible to $\pm$ 2%. The tendency in the chloride ion results is towards an increase in D22 with increasing external salt concentration and this appears more clearly in the tortuosity scaled results. These findings are in accord with previous studies of coion diffusion in AMF - A 104 membranes by Crabtree and Glueckauf (52) and Christensen (51). Agreement in the absolute values of D22 is good with Christensen's sodium chloride data ($D_{22} = 1.69 \times 10^{-7}$ $cm^2 sec^{-1}$ at 0.1 M external sodium chloride and 1.95×10^{-7} $cm^2 sec^{-1}$ at 1.0 molar) but poor with that of Crabtree and Glueckauf. The pattern of increasing coion self diffusion coefficients with increasing salt concentration is however not general. A number of workers have found decreasing coion self diffusion coefficients with increasing salt concentration (54)(63)(64) while others have found the trend exhibited here (37)(65).

The self diffusion coefficients of ions in aqueous solutions show a decrease with increasing salt concentration (66)(67) and so, if the solution analogy holds, this might be the expected behaviour in the membrane. There are two possible explanations, not necessarily mutually exclusive, of the observed trend. The first, (52)(68), regards the effect as a consequence of the overall inhomogeneity of ion exchange resins. The coions are considered to be concentrated in areas of lower than average fixed charge density and tend to diffuse from one such area to another. The overall tortuosity factor for coions is therefore on average higher than the mean value for the whole membrane and so the coion diffusion coefficient is low. As the external salt concentration increases, the concentration of coions becomes significant in more and more volume elements of the exchanger with the result that the diffusing coions can take a more direct route through the membrane. The increase in D_{22} from this source might well be sufficient to swamp out the otherwise expected decrease. The other possibility is that the observed behaviour is caused by a real increase in coion mobility. Such a postulate requires some kind of ion-pairing which involved the coion. In a discussion of electrolyte uptake such ion-pairing has been proposed by Gustafson (69)(70) and compared with analogous phenomena in aqueous polyelectrolytes. The essential postulate is that coion-counterion ion-pairing occurs close to the polymer chains and exerts its greatest influence on coion behaviour at low external concentration. Thus D_{22} would be expected to be abnormally low when a substantial fraction of coion was bound up in ion-pairs.

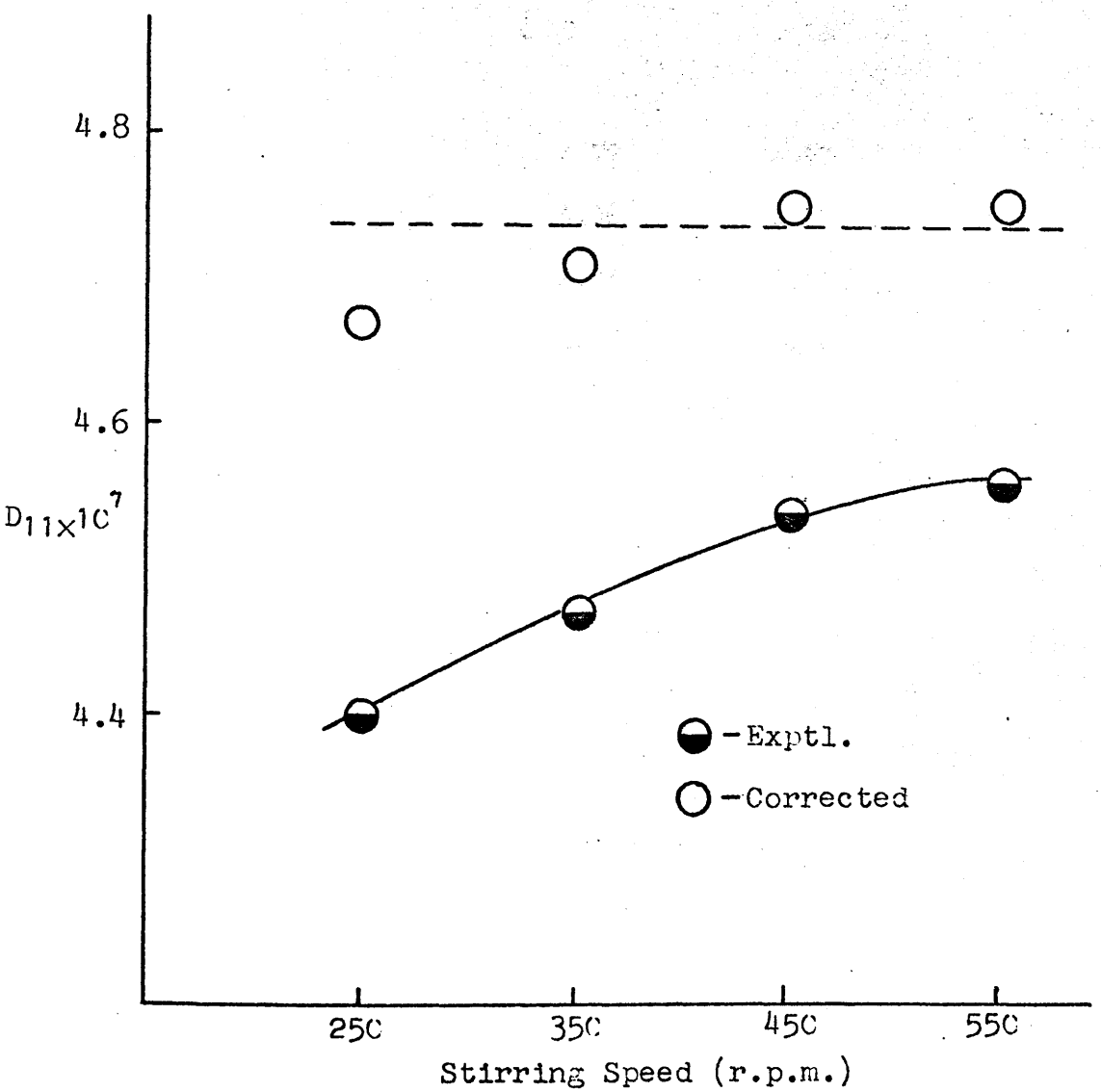


Fig. 4.3 Effect of stirring speed on counterion self diffusion coefficients - Scattergood and Lightfoot correction

TABLE 4.4

COUNTERION SELF DIFFUSION RESULTS

EXTERNAL CONCENTRATION	D_{11} ($cm^2 sec^{-1}$) x 10^7	$D_{11}.\theta$ ($cm^2 sec^{-1}$) x 10^6
0.1 M NaCl	4.77	4.93
0.5 M NaCl	5.06	6.40
1.0 M NaCl	4.58	6.94
2.0 M NaCl	4.10	6.41
0.1 M NaI	0.260 (0.240)	0.752

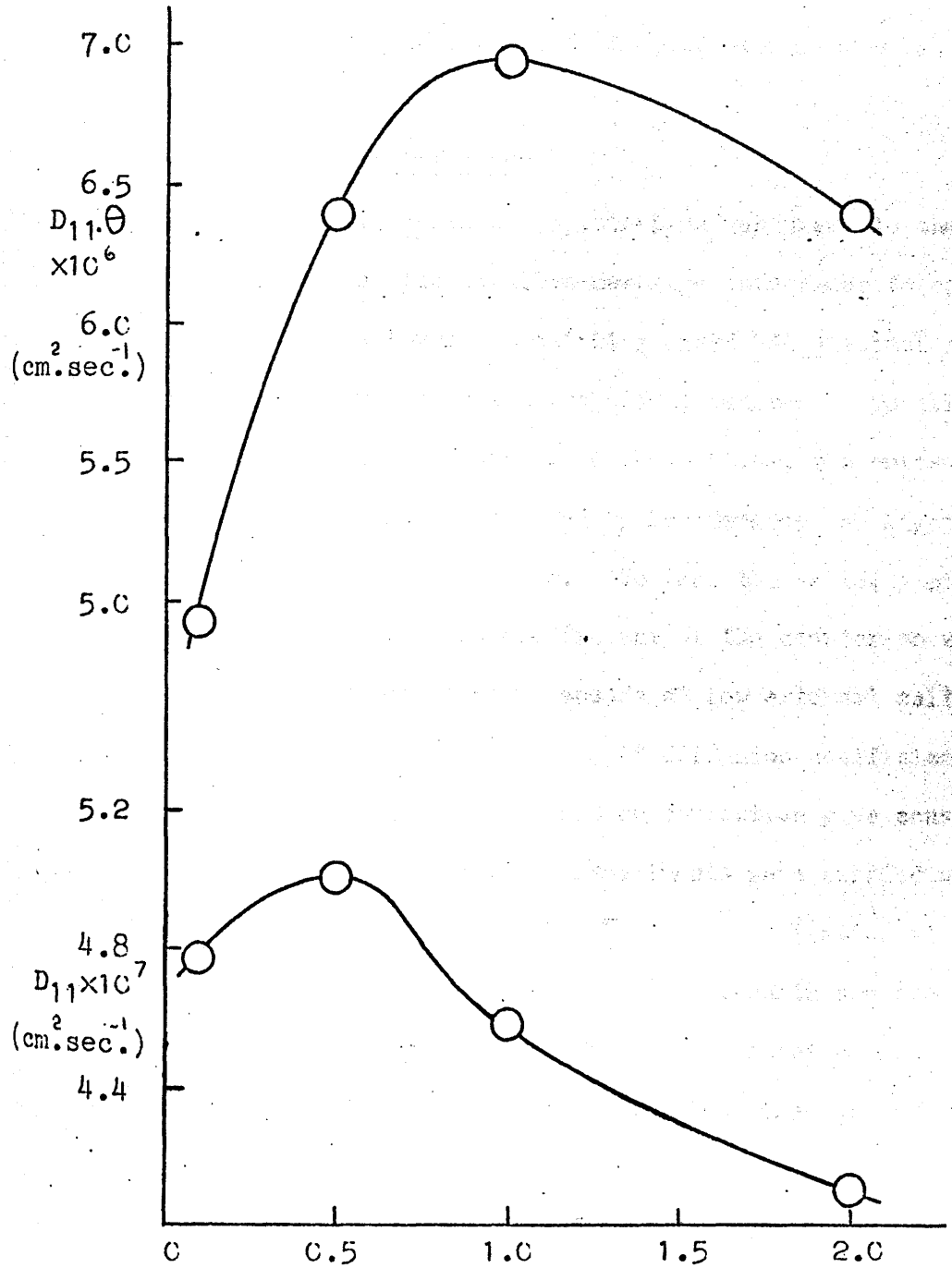


Fig. 4.4 Counterion Self Diffusion Coefficients

From the diffusion data alone there is no way of discriminating between the two views. Suffice to say that either will account for the increase in D_{22} with increasing salt concentration. In Chapter 6 the matter will be raised again and the evidence offered by electron micrographs examined.

4.2.4 Counterion Self Diffusion

In the introduction to Section 4.2, attention was drawn to the importance of 'unstirred films' at the solution-membrane interfaces in counterion self diffusion. The lower the stirring speed and external salt concentration the more important the effect becomes. To allow for the resultant partial rate control of these films, the correction to self diffusion coefficients proposed by Scattergood and Lightfoot (28), discussed in Appendix A.4, was used. To test the validity of the correction, the self diffusion coefficient of the counterion was measured over a range of stirring speeds at low external salt concentration. Under these conditions the apparent self diffusion coefficients measured at the various stirring speeds should on correction give constant membrane diffusion coefficients. Experiments were carried out with 0.1 molar sodium chloride external solution concentration at stirring speeds of 250, 350, 450 and 550 r.p.m. The results are shown in figure 4.3 and the corrected coefficient is constant within the experimental error. At higher external salt concentrations the correction was smaller and fell to approximately 0.2 per cent at 2.0 molar. All other self diffusion coefficients were obtained at a stirring speed of 550 r.p.m. and the results are shown in Table 4.4 with the chloride results additionally plotted in figure 4.4. The value in brackets beside the iodide self diffusion coefficient is that obtained from the non steady

state diffusion experiments performed on the iodide form.

In figure 4.4 a maximum in D11 is observed in both the tortuosity corrected and uncorrected values. This must result from the interplay of several opposing factors and it is of some interest to consider the possible causes. Counterion self diffusion has been the subject of much investigation (see for example (6)(47)(58))and various workers have found increasing trends, decreasing trends and maxima in the variation of D11 with increasing external concentration. As in coion self diffusion it is more difficult to explain an increase than a decrease in the self diffusion coefficient with increasing salt concentration. In aqueous sodium chloride solutions, the chloride self diffusion coefficient decreases with increasing salt concentration (66)(67) and it might again be reasonable to expect similar behaviour in the membrane. Path tortuosity, if a correction has not been included in the calculations, would predict the same trend. Spiegler (71) has suggested that while exchanger phase diffusion coefficients should decrease with increasing concentration, resin inhomogeneity may produce the opposite effect - an argument which closely parallels that for the coions (Section 4.2.3).

At low external concentrations the counterions will be concentrated in areas of high fixed charge density which will probably also have a high degree of crosslinking. Obstruction of counterions in these regions will be considerable and so diffusion will be slow. As the external concentration increases, so will the salt uptake. The invading electrolyte will tend to concentrate in the areas of low crosslinking and, since the obstruction in these areas is less, the overall counterion self diffusion coefficient will show an increase.

Just as the resin inhomogeneity argument can be applied to both coion and counterion so also can the ion association argument. Moreover quaternary ammonium-halide ion association is better established than that between coion and counterion, which enhances the attractiveness of this explanation. A completely different approach has been proposed by Jakubovic, Hills and Kitchener (60), based on the polyelectrolyte nature of resins. The authors point out that diffusion of counterions in the electrical double layer close to and parallel to the polyelectrolyte chains in the exchanger will be favoured as their electrostatic potential will be minimised in this region. The overall mobility of the counterion in what has been termed 'chain diffusion' will then depend on the distance between the potential energy minima of the fixed sites and the relative proximity of polymer segments to each other. In a highly swollen resin it is not difficult to imagine that the 'jump' from one chain to another, 'volume diffusion', would be the rate determining step and thus an increase in counterion self diffusion coefficient with increasing external concentration would be predicted by this model. Another related suggestion has been made by Schlögl (63) on the role of the coion in counterion self diffusion. He proposes that the electric fields of the sorbed coions help to bridge the gap between the fields of the polymer chains and so enhance counterion diffusion.

As will be appreciated there are no lack of qualitative explanations of trends in self diffusion coefficients, but the undoubted complexity of diffusion processes in ion exchangers has so far prevented the

development of a useful quantitative theory, and moreover it is rather difficult to assess the significance of the various possible rationalisations of the same diffusion results. It does seem clear however that quaternary ammonium-iodide ion pairing is very important. The iodide self diffusion coefficient is eighteen times smaller than that of the chloride at the same external salt concentration. The lower water content in the iodide form causes the path tortuosity to be higher but the water diffusion experiments indicate that this only removes a factor of between two and three, leaving an additional factor of about seven to be accounted for. In solution, the ratio of the single ion conductances at infinite dilution, $\lambda_o^{Cl^-} : \lambda_o^{I^-}$, is only 0.99:1 (72) and it is therefore apparent that the iodide ions are being strongly retarded by the matrix and the most obvious cause of this would be a strong quaternary ammonium-iodide interaction. The mere fact that the water content falls so sharply from the chloride to the iodide form is in itself strongly indicative of some such effect. The osmotic or swelling pressure, $\overline{\Pi}$, is defined as (73)

$$\overline{\Pi} = - \frac{RT}{Vw} \ln(\bar{a}_w / a_w) \qquad (4.6)$$

where $\bar{a}_w$ and a_w are the water activities in the membrane and solution phase respectively and Vw is the partial molar volume of the water. When the solution is changed from 0.1 molar sodium chloride to 0.1 molar sodium iodide, Vw and a_w scarcely alter, yet the iodide form deswelling is much greater than might be predicted merely on the basis of different hydrated ionic sizes. In more specific terms

$$\overline{\Pi} \text{ (chloride form)} > \overline{\Pi} \text{ (iodide form)} \qquad (4.7)$$

and therefore $\bar{a}_w$ (chloride form) $<$ $\bar{a}_w$ (iodide form) (4.8)

TABLE 4.5

CONDUCTIVITY RESULTS

EXTERNAL CONCENTRATION	SPECIFIC CONDUCTIVITY ($\bar{K}$) $(ohm^{-1}\ cm^{-1}) \times 10^{3}$
0.1 M NaCl	3.41
1.0 M NaCl	3.06
0.1 M NaI	0.242

Now the lower the water activity in general, the larger the number of solute particles in solution (a consequence of Raoult's Law) so the deduction from equation 4.8 would be that there are fewer solute particles present in the iodide form, which would again point strongly towards ion association.

A comparison of the coion diffusion coefficients in the two systems shows that, after due allowance is made for tortuosity, the sodium ions appear to be diffusing eight and a half times more slowly in the iodide form. Although the electrolyte uptakes at 0.1 molar external solution concentration have a fairly large error, the effect is too large to be accounted for by this alone. If there is a considerable degree of quaternary ammonium-iodide ion pairing, salt exclusion by the membrane would be expected to be less efficient and coion-counterion interactions less important. Consequently it would be predicted that tortuosity scaled coion self diffusion coefficients would be higher in the iodide form than in chloride form at the same external salt concentration. This is patently not so, and it would seem that the coion is subject to considerable extra retardation. In the next chapter the results of applying non equilibrium thermodynamics to the transport experiments will be presented and the evidence for and against ion pairing in the chloride and iodide forms examined in this light.

4.3 Conductivity

Conductivities in three systems, the membrane in equilibrium with 0.1 molar and 1.0 molar sodium chloride and 0.1 molar sodium iodide, were measured (Table 4.5) and consequently no extended discussion of the

variation of membrane specific conductivities with external salt concentration is possible. Predictions of specific conductivities in all the systems studied are however available from the Nernst-Planck flux equations as discussed in Chapter 2, but as these require a knowledge of the other transport data, this particular aspect of the conductivities will be dealt with in the next chapter.

Ionic concentrations in the membrane phase are so high that it is extremely difficult to find any suitable aqueous solution data on a likely model salt to allow comparisons between the two. Conductivities in aqueous solutions however have been studied intensively over a considerable range of concentrations. Most inorganic salts are not soluble up to the molarities encountered in the membrane but the simple quaternary ammonium halides are, and conductivities have been measured close to the lowest membrane concentration. Molenat (74) has measured the conductivity of tetramethylammonium chloride in the range 0.183-5.60 molar and at the latter concentration obtains a value for the specific conductivity of 5.85×10^{-2} ohm^{-1} cm^{-1}. If this value is divided by the tortuosity factor for the membrane in 0.1 molar sodium chloride, 10.3, the resultant specific conductivity is 5.65×10^{-3} ohm^{-1}cm^{-1}. The experimental value in the 0.1 molar sodium chloride system is 3.41×10^{-3} ohm^{-1}cm^{-1}. The agreement is impressive, all the more so when it is considered that the membrane ionic concentration is 6.23 molar and that the specific conductivity of the model solution is decreasing with increasing concentration. A more complete study of the transport properties of the simple tetraalkylammonium halides might well prove them to be very useful model systems for anion exchangers of similar type.

TABLE 4.6

WATER TRANSFERENCE NUMBER RESULTS

EXTERNAL CONCENTRATION	t_3
0.1 M NaCl	- 4.18
0.5 M NaCl	- 3.84
1.0 M NaCl	- 3.48
2.0 M NaCl	- 3.07
0.1 M NaI	- 2.08

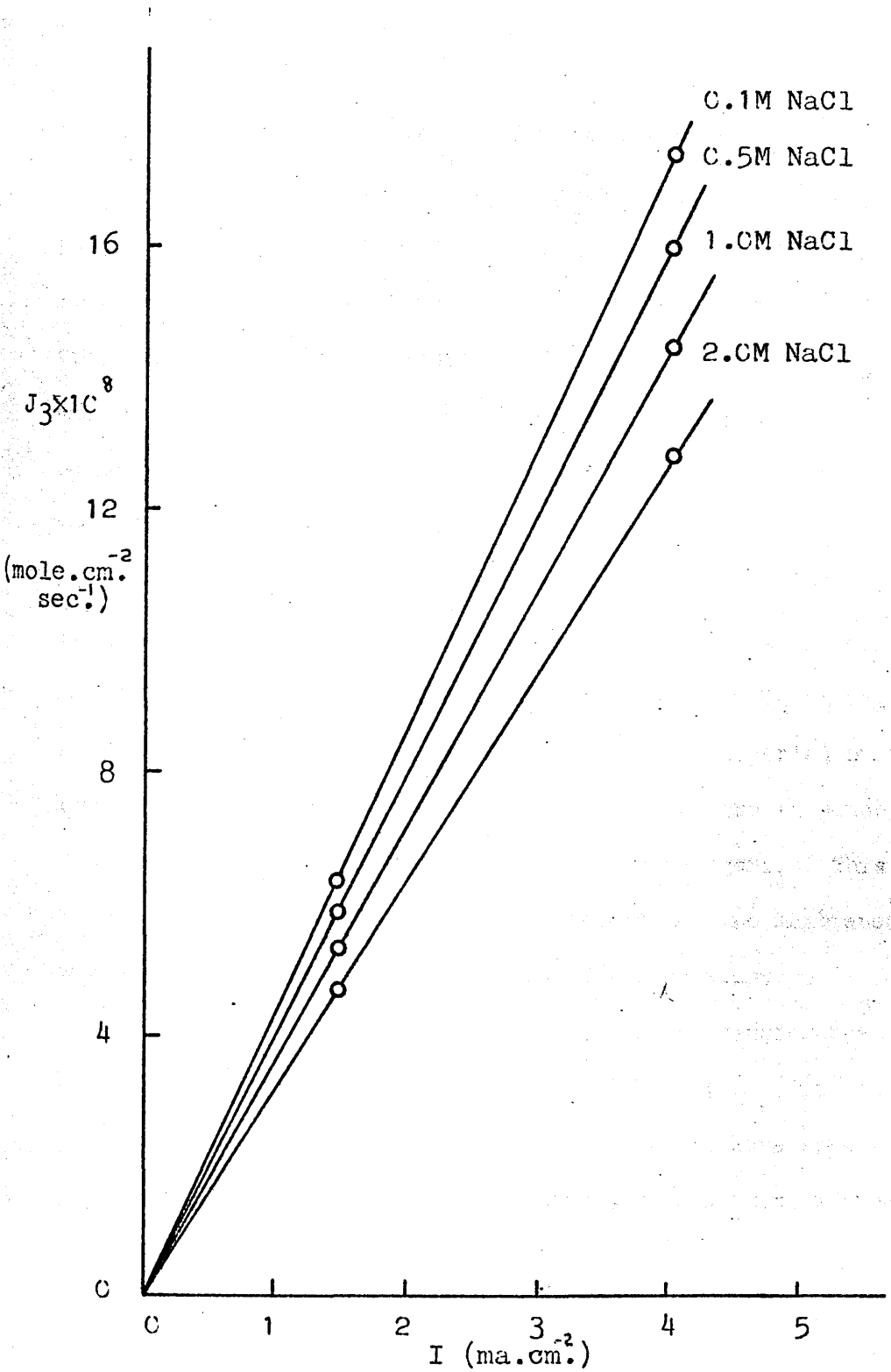


Fig. 4.5 Dependence of electroosmotic water transport on current density

4.4 Electroosmosis

The electroosmosis results are best dealt with in two parts. Water transference studies in the chloride form were straightforward with no particular difficulties being encountered and are therefore suitable for comparison with other work. The much lower conductivity of the iodide form caused excessive membrane movement in the applied electric field preventing the horizontal capillary method from being useful, and tritium tracer flows with and against the electric current had to be measured to obtain t_3.

The water transference numbers for the various systems studied are shown in Table 4.6. The chloride results show the normal concentration dependence characteristics of t_3 as found by many other workers (47) in that $|t_3|$ falls with increasing concentration (t_3 is negative in anion exchangers as the net flow of water transported by the halide ions is to the anode). The $|t_3|$ obtained here are in general a good deal smaller than those quoted for cation exchangers. This is a direct consequence of the low water contents of the membranes and the interrelated low degree of hydration of halide ions.

One of the more controversial aspects of water transference studies has been the variation of t_3 with current density. The topic has been well reviewed in reference 47. Some authors have found that at external concentrations of 0.1 molar and less, $z_1 t_3$ increases with decreasing current density, but many others have not. The variation of the water flow with current density was examined in this work and the results are shown in Figure 4.5. It will be observed that t_3 is completely independent of current density at all concentrations.

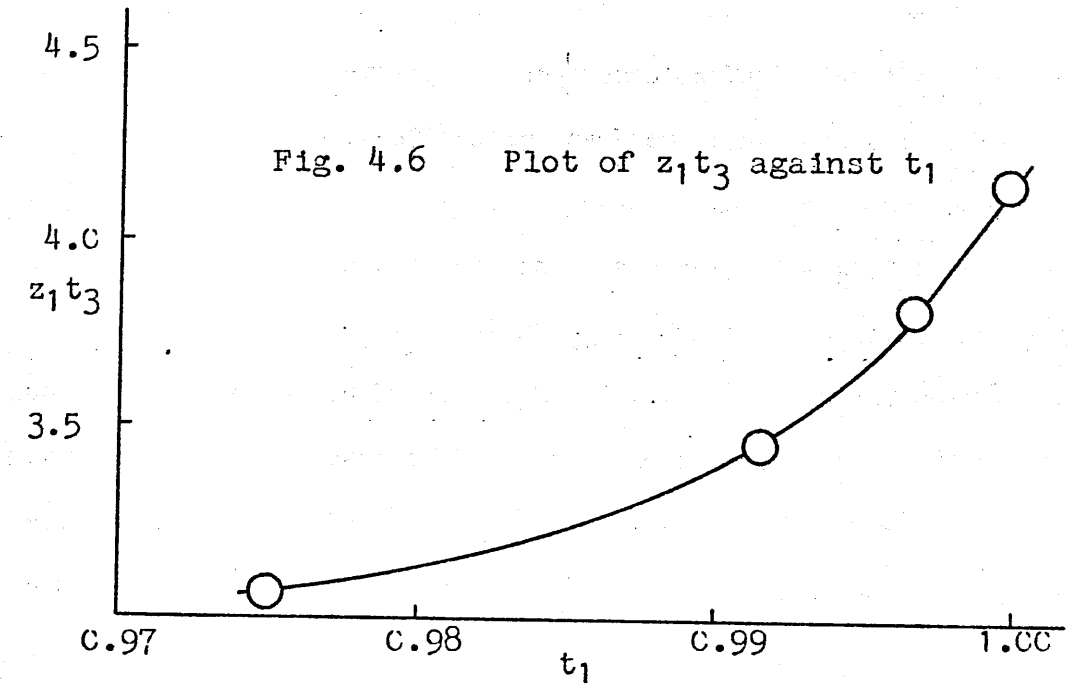


Fig. 4.6 Plot of $z_1 t_3$ against t_1

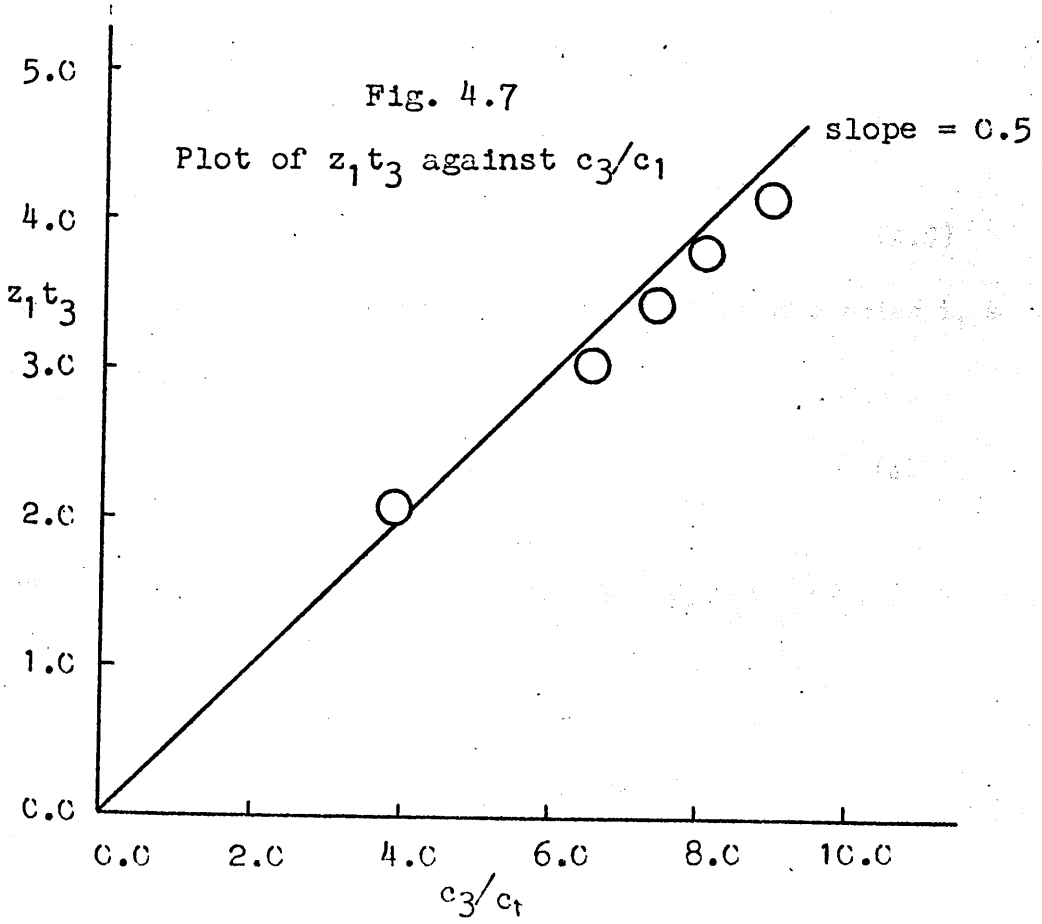


Fig. 4.7

Plot of $z_1 t_3$ against c_3/c_1

In Chapter 2 attention was drawn to the usefulness of a linear t_3-t_1 relationship which permits an unequivocal solution of the phenomenological equations. Such a relationship has been found before by other workers (54)(75)(76) but again it is by no means a general phenomenon. Figure 4.6 shows the results obtained in this work. The plot is strongly curved. A graph of z_1t_3 against c_3/c_1 for all the data,(Figure 4.7) on the other hand, is linear with a gradient of 0.5 and goes through the origin. Such a straight line relationship has been observed before, e.g. as in Spiegler's compilation of data (15), but its origin is of some interest. Several factors are involved. Given a low coion content, then the definition of t_3

$$t_3 = \frac{J_3F}{I} = \frac{J_3F}{(z_1J_1+z_2J_2)F}$$

may be written

$$z_1t_3 = J_3/J_1 \qquad (4.9)$$

Expanding J_i as c_iv_i, where v_i is the velocity of species i, equation 4.9 becomes

$$z_1t_3 = \frac{c_3}{c_1} \cdot \frac{v_3}{v_1} \qquad (4.10)$$

The observation that a plot of z_1t_3 against c_3/c_1 is linear therefore means that in experiments where the external applied force is an electrical potential gradient, the water moves at a constant fraction of the velocity of the counterion. The value of the fraction is a function of several parameters, of which the most important are the degree of hydration of counterion and matrix and the relative magnitudes of

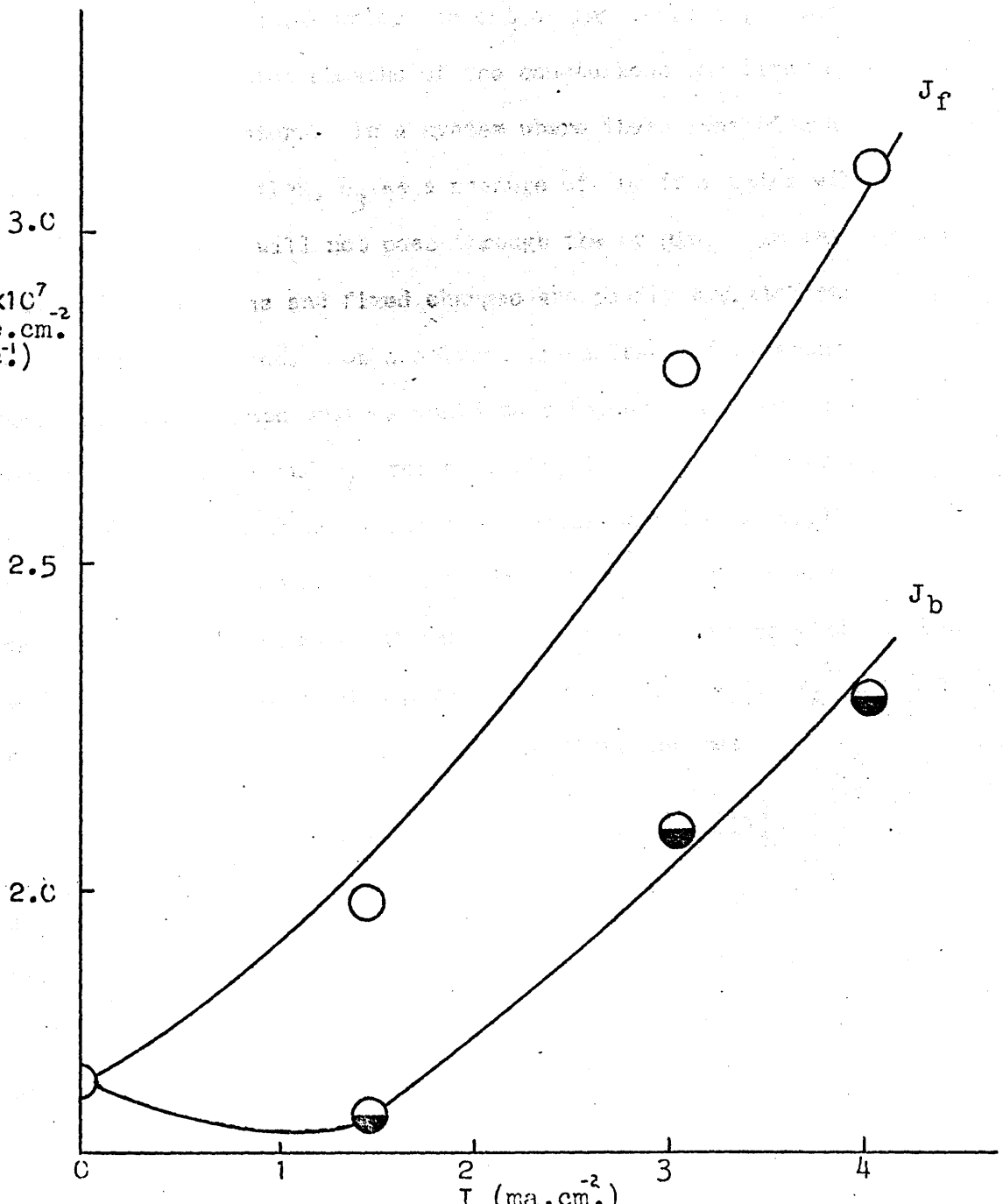


Fig. 4.8 Observed current dependence of forward and back flows of tritiated water in iodide electroosmotic experiments

counterion-water and matrix-water frictional interactions. c_3 as measured gives the total water content of the membrane, comprising water bound in the hydration sheaths of the counterions and fixed charges as well as the free water. In a system where these ions bind a significant amount of water to them, c_3 as a measure of the free water will be too large and the plot will not pass through the origin. In this system, however, counterions and fixed charges are poorly hydrated and the effect can be ignored. On a solvent fixed frame of reference the counterions and fixed charges would tend to move in opposite directions with velocities v_1^1 and v_4^1 respectively, therefore on changing back to the membrane reference frame the counterion velocity will be $v_1 = v_1^1 + v_4^1$ and that of the water $v_3 = v_4^1$. If species 1 and 4 have a similar frictional interaction with water - which will be seen to be so in this system in the next chapter - then $v_1^1 = v_4^1$ and the ration $v_3/v_1 = 0.5$. Equation 4.10 therefore becomes

$$z_1 t_3 = 0.5 \times \frac{c_3}{c_1} \qquad (4.11)$$

as found.

Electroosmotic experiments in the iodide form, which as mentioned had to be performed by measuring tritium tracer flows with and against the electric current, gave puzzling results. The problem lay not in the value of t_3 eventually obtained but in the fact that both forward and back flows of tritium were larger than the self diffusion flow (Figure 4.8). It is perfectly normal for the forward flow to be larger than the self diffusion flow, but not the back flow. Evidently the

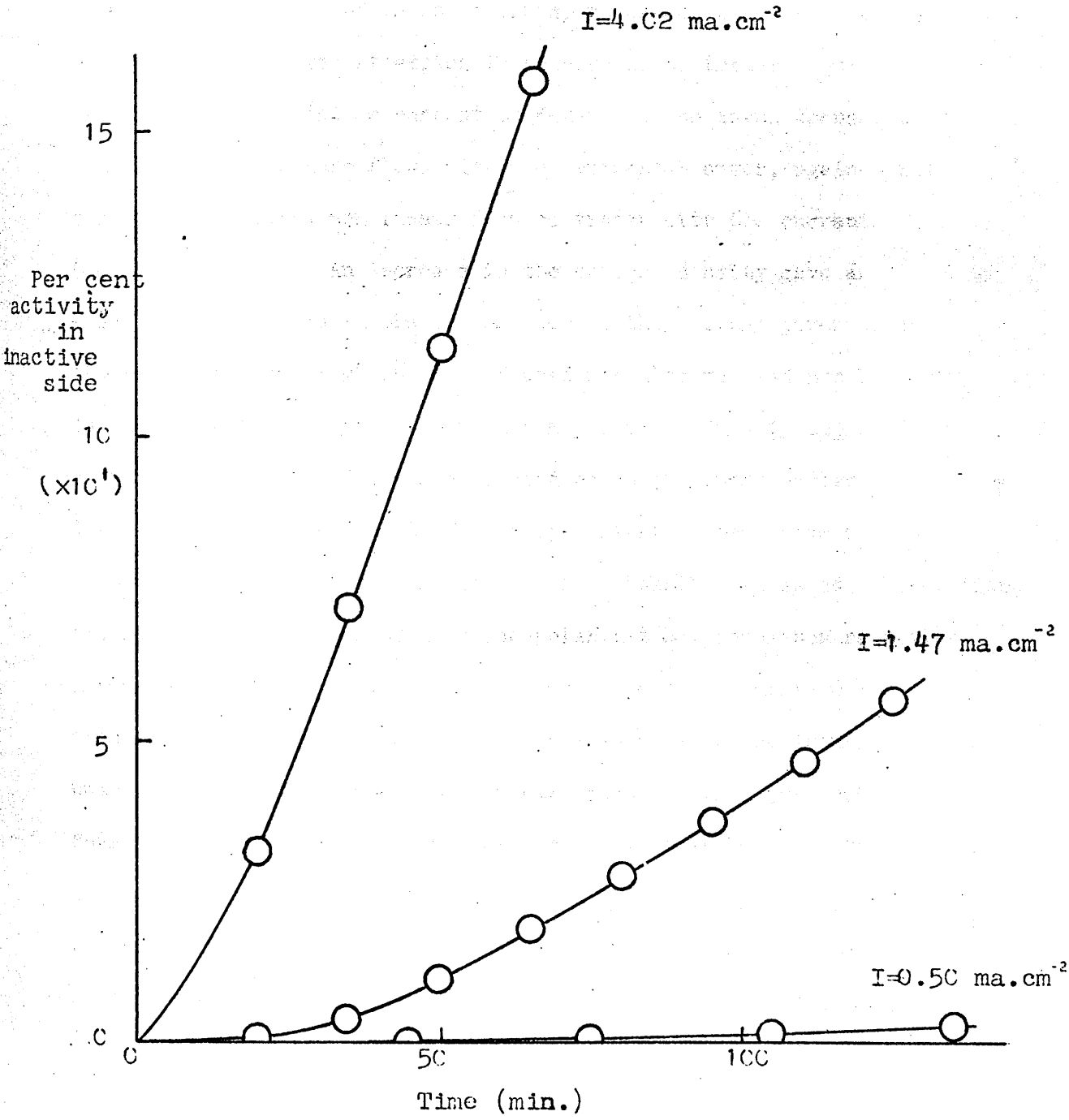


Fig. 4.9 Variation of coion flows with current density in iodide transport number experiments

water molecules become more mobile as the current increases. Further anomalies were observed in coion transport number studies in the same system. When it was attempted to measure coion tracer flows with and against the electric current to determine the coion transport number, there was zero flow, within experimental error, against the current and a large non linear flow of tracer with the current. (See Figure 4.9). An increase in the current density gave an even larger increase in the tracer flow so that at any given time the amount of tracer which had diffused was also related non linearly to the current density. At the maximum current density employed, approximately 4 $ma.cm^{-2}$, the estimated coion transport number was 0.2 - yet e.m.f measurements with a concentration cell gave a value of t_2 of zero within experimental error. Possibly these odd observations are caused by some form of membrane polarization phenomenon resulting in water splitting. Such an effect would certainly explain the electroosmotic behaviour but on the other hand in coion transport number experiments, it might be expected that the hydrogen ions so formed would carry most of the coion current at the expense of sodium ions, which is not in accord with the experimental observations. Polarization as an explanation of the results appears untenable. If the coions are carrying up to 20 per cent of the current with a concentration over two orders of magnitude lower than the counterion, then they must be moving with a considerable velocity. The disruptive effect caused could account for the apparent increase in the water mobility but the basic question remains unanswered. Clearly the whole matter would benefit from further study.

4.5 Transport Numbers

A discussion on coion transport number measurements has been given in relation to the problems encountered in the iodide form. This section will therefore be confined to a discussion of the relatively well behaved chloride results. There are four possible methods of calculation; a) from the net flow of coion (equation 3.5), b) from the flux ratio (equation 2.53), c) from the tracer flow with the electric current $J_2(f)$, combined with the coion self diffusion flow, $J_2(0)$, and d) from the tracer flow against the current, $J_2(b)$, in combination with the self diffusion flow. Expressions for methods c) and d) have been deduced by Meares and Sutton (77). They are

$$t_2 = - \frac{z_2 F J_2(0)}{I} \ln \left(1 - \frac{It_2}{z_2 F J_2(b)}\right) \qquad (4.12)$$

and

$$t_2 = \frac{z_2 F J_2(0)}{I} \ln \left(1 + \frac{It_2}{z_2 F J_2(b)}\right) \qquad (4.13)$$

The advantages of equations 4.12 and 4.13 are that they allow calculation of t_2 in systems where it is very difficult or inconvenient to measure either $J_2(f)$ or $J_2(b)$. The disadvantages are twofold. The first is that for low t_2 values, $J_2(0)$ and $J_2(b)$ tend to be little different and the results obtained from equation 4.13 therefore become erratic. The fact that the data required, $J_2(0)$ and $J_2(f)$ or $J_2(b)$, has to come from two different experiments is in itself a drawback. The second disadvantage is that neither equation can be easily solved for t_2. The procedure adopted was to select a value of t_2 and compare the right and left hand sides of the relevant equation. Only at the t_2 value appropriate to the input data is there equality. The problem

TABLE 4.7

CALCULATION OF TRANSPORT NUMBERS

EXTERNAL CONCENTRATION	Jo mole $cm^2 sec^{-1}$ x 10^{10}	Jf mole $cm^2 sec^{-1}$ x 10^{10}	Jb mole $cm^2 sec^{-1}$ x 10^{10}
0.1 M NaCl	0.1365	0.1862	0.0627
0.5 M NaCl	1.557	2.392	0.9678
1.0 M NaCl	4.317	6.751	3.158
2.0 M NaCl	11.23	17.99	7.636

CALCULATION OF COION TRANSPORT NUMBER t_2

	From JNET	From Flux Ratio	From Jo and Jf	From Jo and Jb
0.1 M NaCl	0.0003	0.0004	0.0002	0.0005
0.5 M NaCl	0.0034	0.0034	0.0035	0.0033
1.0 M NaCl	0.0086	0.0079	0.0101	0.0062
2.0 M NaCl	0.0248	0.0231	0.0277	0.0196

is one particularly suited to solution by a computer and the program written can be found in Appendix A.6. Given a starting guess of t_2, the program executes a series of cycles in which the guess is systematically improved until the values of the right and left hand sides of the equation agree to within a pre-specified deviation. The flux ratio expression, equation 2.53 requires $J_2(f)$, $J_2(b)$ and $J_2(0)$ whereas the calculation of t_2 from the net flow expression, equation 3.5, requires only $J_2(f)$ and $J_2(b)$, both of which are determined in the same experiment. For these reasons the values of t_2 ultimately employed in calculations of phenomenological coefficients in Chapter 5 were those obtained from equation 3.5. It is nevertheless interesting to compare the values from the different methods of calculation as they provide a useful check on the self consistency of the data. The data and results are shown in Table 4.7. Some idea of the efficiency of the membrane can be gained by the fact that even at an external sodium chloride concentration of 2.0 molar, the counterion transport number is still greater than 0.97. Agreement between values of t_2 calculated from the net flow and flux ratio expressions are in general good, (as one would hope) but a fair scatter is evident in the values calculated from equations 4.12 and 4.13. Not surprisingly these values span the net flow and flux ratio values and they simply reflect the experimental difficulties encountered in the system.

TABLE 4.8

SALT AND OSMOTIC FLOWS

CONCENTRATION CELL	$\left(-\frac{\partial u_3}{\partial x}\right)$ joule mole^{-1}cm^{-1} x 10^{-2}	Jw mole cm^{2}sec^{-1} x10^8	$\left(-\frac{\partial u_2}{\partial x}\right)$ joule mole^{-1}cm^{-1} x10^5	Js mole cm^{2}sec^{-1} x10^{11}
0.15/0.05m NaCl	3.481	1.185	2.130	2.970
1.5/0.5m NaCl	38.08	7.447	2.298	72.27
0.15/0.05m NaI	3.718	0.2057	-	-

4.6 Salt and Osmotic Flows

If two aqueous solutions of different concentrations of the same electrolyte are separated by an ion exchange membrane, chemical potential gradients are set up which tend to transport salt from the concentrated solution to the dilute and water in the reverse direction. The complex interactions which ensue have already been described in terms of non equilibrium thermodynamics in Sections 2.2.1.4 and 2.2.1.5.

The results of the osmotic flow experiments are shown in Table 4.8. It is observed that while the force acting on the water in the 1.5/0.5 molal sodium chloride cell is just over ten times that in the 0.15/0.05 molal sodium chloride cell, the osmotic flow is only larger by a factor of six. This is a result of the lower water content of the membrane at the higher concentration and the consequent reduced mobility of the water caused by increased path tortuosity. The coion is not present in sufficient concentration for water-salt coupling to have a marked effect on the water flow. A similar analysis is possible for the 0.15/0.05 molal concentration cells in the chloride and iodide forms where the forces on the water are essentially identical. The salt flow results, also in Table 4.8, show that there is an increase of almost thirty times in the salt flow from the 0.15/0.05 molal concentration cell to the 1.5/0.5 molal cell, despite the similar forces. The main cause of this is the large increase in coion concentration as Donnan exclusion becomes less efficient.

CHAPTER 5

APPLICATION OF TRANSPORT THEORIES

Combination of the conductivity, transport numbers, water transference number, salt flow and osmotic flow results permits an estimate of the non equilibrium thermodynamic phenomenological coefficients. However the application of non equilibrium thermodynamics to membrane transport processes in the steady state under isothermal and isobaric conditions defines five independent equations in terms of six unknown phenomenological coefficients. Certain assumptions must therefore be made as to the relative magnitude of coefficients. The solution of the coefficient matrix without making assumptions requires the use of pressure as a thermodynamic force. Experimental difficulties attend measurements in membrane systems with applied pressure gradients (78) and with a tight membrane such as that used in this work, the required pressure gradient would be large enough to make destruction or deformation of the membrane almost certain. It was therefore decided to concentrate on critical examination of the various assumptions which may be utilised as the sixth equation. Some of the assumptions have good theoretical backing while others rely more on 'chemical intuition' derived from a close study of solution data and other membrane results. This makes it possible to attempt a value judgement of the 'intuitive' assumptions while still giving a reliable set of coefficients for general discussion. The first task is however to consider possible assumptions and this will be done in Section 5.1. Section 5.2 is a general discussion of the results of the type indicated above. A complete set of phenomenological coefficients in conjunction with self diffusion data

allows calculation of the isotope-isotope cross coefficients and in Section 5.3 the available evidence on isotope-isotope interactions from this and other studies will be examined. Section 5.4 deals with the application of the Nernst-Planck flux equations to the electrical experiments.

5.1.1 Assumptions Based on Self Diffusion Coefficients

A non equilibrium thermodynamic treatment of self diffusion has already been given in Section 2.2.3 and it was shown that the self diffusion coefficient of a mobile species i, D_{ii} can be expressed (in the presence of isotope-isotope interaction) as

$$D_{ii} = \frac{RT}{c_i(R_{ii} - R_{ii}')} \qquad (5.1)$$

To make use of self diffusion coefficients as a direct measure of Rii therefore requires formally that $R_{ii}' = 0$ but given the existence of experimental error, it is sufficient that the isotope-isotope term R_{ii}' be insignificant compared to R_{ii}, i.e. 1% or less. In this study the self diffusion coefficients of the counterion (chloride and iodide), coion (sodium) and water, D_{11}, D_{22} and D_{33} respectively were measured offering three possible assumptions. Before considering each in turn, some further analysis of the term $c_iR_{ii} - c_iR_{ii}'$ is necessary. c_iR_{ii} measures the friction between one mole of i and the existing concentrations of all other species except i in the membrane phase (Section 2.2.2). This is brought out clearly in the expansion of c_iR_{ii} in terms of equation 2.40 when

$$c_iR_{ii} = -\sum_{j=1}^{4} c_jR_{ij} \quad (j \neq i) \qquad (5.2)$$

$c_i R_{ii'}$ on the other hand measures the friction of one mole of isotope i' with those i per unit volume at the concentration existing in the exchanger. At a molecular level, this term reflects the relative importance of i - i kinetic interactions while $c_i R_{ii}$ measures those of i with all other species (see Section 5.3). The term kinetic interaction is used here to denote any interaction which causes a change in velocity of the particles concerned. This widens the definition to include long range coulombic and van der Waal interactions as well as the conventional 'billiard ball' type of collision. The strong tendency of water molecules to form hydrogen-bonded clusters and the observation that water is the major constituent of the pore solution, would suggest on the basis of the above arguments that $R_{33'}$ is not a negligible fraction of R_{33}. Indeed, in total, water-water interactions may well be at least as important as the ion-water interactions in determining the diffusional behaviour of a water molecule. The assumptions that $R_{11'}$ and $R_{22'}$ are negligibly small compared to R_{11} and R_{22} respectively were made implicitly by Spiegler (15) in his theoretical scheme to determine $\bar{X}ik$ frictional coefficients and so have a precedent in the literature. $R_{11'} = 0$ must however be considered a dubious assumption since there is a high concentration of counterions in the pore liquid. Any given counterion is likely to be measurably influenced by kinetic interactions with other counterions and recent work by Scattergood and Lightfoot (28) on AMF C-103 and Gardner and Paterson (79) on AMF C-60 cation exchange membranes have emphasised the importance of $R_{11'}$. On the other hand $R_{22'} = 0$ is much more promising. In the system under study, coion is

present only to 0.1 per cent of the counterion at 0.1 molar and 3.6 per cent at 1.0 molar sodium chloride. 2-2 kinetic interactions must therefore be very infrequent compared to 2-1, 2-3 and 2-4 and consequently isotope-isotope interactions may well be neglected. The relative importance of $R22'$ should increase, however, with increasing coion uptake and eventually the assumption $R_{22}' = 0$ may cease to be useful, but given the uptakes encountered in this work, it seems very powerful.

5.1.2 Mobility Coefficient Assumptions

These are all based on the concentration dependence of ℓ_{ik} cross coefficients first demonstrated by Miller (19) in binary electrolyte solutions where the cation-anion cross coefficient L_{12} tends to zero as the solution approaches infinite dilution. In the system studied here, the minute concentrations of coion present make the assumptions $\ell_{12} = 0$, $\ell_{23} = 0$ or all $\ell_{2k} = 0$ seem realistic. The last of these is equivalent to ignoring coion completely and treating the system as comprising species 1, 4 and 3 of a 1:1 electrolyte solution - the binary approximation. This was the only reasonable way to treat the iodide results as the extremely low coion concentration ($c_2/c_1 < 1/1000$) made the measurement of coion flows almost impossible. At this concentration, however, the influence of coion on the behaviour of the other mobile species would undoubtedly be negligible. The separate assumptions $\ell_{12} = 0$ or $\ell_{23} = 0$ are by nature unbalanced as either results in all the 2-1 and 2-3 interactions being absorbed into the remaining ℓ_{2k} coefficient and ℓ_{22}. Consequently misleading results can be obtained on inverting the ℓ-coefficient matrix to give R coefficients as the latter, being on a mole to mole basis, magnify the imbalance. Miller himself has stated his dislike of setting ℓ_{ik} cross coefficients

equal to zero in his paper on ternary systems (80) but this is not sufficient reason to discard such assumptions out of hand. In fact, on examination, the assumption $\ell_{23} = 0$ seems particularly good for ℓ coefficients (although matrix inversion for the R coefficients still suffers the disadvantage mentioned above). Consideration of the five ℓ coefficient equations

$$t_1 = (z_1^2\ell_{11} + z_1z_2\ell_{12})/\alpha \qquad (2.24a)$$

$$t_2 = (z_2^2\ell_{22} + z_1z_2\ell_{12})/\alpha \qquad (2.24b)$$

$$t_3 = (z_1\ell_{13} + z_2\ell_{23})/\alpha \qquad (2.26)$$

$$J_3 = (\ell_{13} - \frac{t_1}{z_1} t_3\alpha)(-\frac{\partial u_{12}}{\partial x}) + (\ell_{33} - t_3^2\alpha)(-\frac{\partial u_3}{\partial x}) \qquad (2.35)$$

$$J_s = (\ell_{11}\ell_{22} - \ell_{12}^2)/\alpha \cdot (-\frac{\partial u_{12}}{\partial x}) + (\ell_{13} - \frac{t_1}{z_1} \cdot t_3\alpha)(-\frac{\partial u_3}{\partial x}) \qquad (2.38)$$

shows that ℓ_{23} appears only in the t_3 expression. The dependence of ℓ_{ik} cross coefficients on concentration means that $\ell_{13} \gg \ell_{23}$ as $c_1 \gg c_2$, and even though ℓ_{12}, ℓ_{22} and ℓ_{23} are commensurate in magnitude, neglect of ℓ_{23} will scarcely affect the values of the other five. Similarly the neglect of ℓ_{12} will be unimportant in equations 2.24a and 2.38 but in equation 2.24b there could be a large effect on ℓ_{22}. The concentration dependence of ℓ_{13} and ℓ_{23} suggests the further relation

$$\ell_{13}/c_1 = \ell_{23}/c_2 \qquad (5.3)$$

i.e. coupling between sodium and water is very similar to that between chloride and water. This is not entirely unreasonable as both are ion-dipole interactions, but at best equation 5.3 can only be considered as an order of magnitude estimate of ℓ_{23}. The kind of relation typified by equation 5.3 does have some support from the literature

where Miller (80) uses similar relations with success to calculate L coefficients in ternary systems from those of constituent binaries.

The consequences of equation 5.3 on the solvent fixed mobility coefficients are interesting. From equations A.1.13 and A.1.14 in Appendix A.1 equation 5.3 can be expanded as

$$\frac{\ell_{13}}{c_1} - \frac{\ell_{23}}{c_2} = 0 = \frac{c_3}{c_4}\left(\frac{L_{24}}{c_2} - \frac{L_{14}}{c_1}\right) \qquad (5.4)$$

$$\text{i.e. } L_{14} / c_1 = L_{24} / c_2 \qquad (5.5)$$

In ternary mixtures of electrolytes Miller has always found L_{24} to be negative and L_{14} always positive, and so if the solution analogy holds in the exchanger, equation 5.3 looks less promising.

5.1.3 Frictional Coefficient Assumptions

Two possible R coefficient assumptions which have appeared in the literature are $R_{12} = 0$ and $R_{23} = 0$. The first of these is due to Spiegler (15) and was the explicit assumption made to solve the $\bar{X}_{ik}$ frictional coefficient matrix, the justification being that for low coion uptakes, coion-counterion friction would be small enough to be neglected. This has not gone unchallenged by other authors (34)(81) and, in general, since R coefficients measure friction on a mole to mole basis, setting them to zero seems intrinsically unsatisfactory. The assumption $R_{23} = 0$, first proposed by Staverman (81), may well be preferable to neglecting R_{12} since the ion-dipole friction would be smaller than that between coion and counterion. A further relationship between R coefficients arises from a rearrangement of equation 2.41c;

TABLE 5.1

PREDICTED SIGNS (All ℓ_{ij} positive i=1-3, j=1-3).

	R_{11}	R_{12}	R_{22}	R_{13}	R_{23}	R_{33}
Theoretical (Kedem)	+	-	+	-	-	+
$\ell_{12} = 0$	⊕	+	⊕	-	-	+
$\ell_{23} = 0$	+	-	⊕	-	+	⊕
$R_{12} = 0$ (Spiegler)	⊕	zero	⊕	-	-	⊕
$R_{23} = 0$ (Staverman)	⊕	-	⊕	-	zero	⊕

O = No prediction from assumption

⊕ = From O.R.R.

$$(0 = \frac{t_1}{z_1} R_{13} + \frac{t_2}{z_2} R_{23} + t_3 R_{33}) .$$

With $z_1 = -1$, $z_2 = +1$ and $t_2 = 1-t_1$ the equation becomes

$$t_3 = \left(\frac{R_{13} + R_{23}}{R_{33}}\right) t_1 - \frac{R_{23}}{R_{33}} \qquad (5.6)$$

A linear $t_3 - t_1$ relationship would therefore provide an identity between R coefficients without recourse to assumptions (79) and an unambiguous solution would be obtained. No such linear relation was found in this work (figure 4.6).

Sections 5.1.1-5.1.3 list some of the possible assumptions which can be made to permit solution of the phenomenological coefficients. Of these mentioned, sets of ℓ and R coefficients were calculated for $R_{11}' = 0$, $R_{22}' = 0$, $\ell_{12} = 0$, $\ell_{23} = 0$, all $\ell_{2k} = 0$, $R_{12} = 0$ and $R_{23} = 0$ at 0.1 and 1.0 molar sodium chloride. Before proceeding to a discussion of the results set out in Tables 5.2 to 5.5 it is worthwhile to elaborate on a point raised in section 5.1.2. Attention was drawn to the fact that setting an individual ℓ_{2k} coefficient to zero caused imbalance in the resulting ℓ and R coefficients. The same is true of the assumptions $R_{12} = 0$ and $R_{23} = 0$ and the net effect is that the changes of sign evident in R_{12} and R_{23} are not entirely arbitrary. This can be demonstrated by inverting an ℓ matrix with each of the assumptions in turn, to determine the signs of the resultant R coefficients. Table 5.1 shows the consequences if all the ℓ coefficients are positive. Thus $\ell_{12} = 0$ will automatically give the 'wrong' sign for R_{12} and the 'correct' ones for R_{23} and R_{13}. (The basis for deciding whether or not the sign is 'correct', was Kedem's hypothesis (25) which stated that R coefficients between attractive species are negative and those between repulsive species

TABLE 5.2

0.1 molar NaCl FRICTIONAL COEFFICIENTS

ASSUMPTION	R_{11} x10^{-12}	R_{12} x10^{-11}	R_{22} x10^{-15}	R_{13} x10^{-11}	R_{23} x10^{-11}	R_{33} x10^{-10}	R_{14} x10^{-12}	R_{24} x10^{-12}	R_{34} x10^{-11}	R_{44} x10^{-12}
$\ell_{23}=0$ and matrix inversion	+3.24	-6.99	+7.13	-1.22	+0.26	+2.91	-2.15	-9.73	-1.38	+3.40
$\ell_{13}/c_1=\ell_{23}/c_2$ and matrix	+3.22	+10.3	+6.96	-1.18	-4.00	+2.81	-2.18	-7.42	-1.32	+3.37
$\ell_{12}=0$ and matrix	+3.58	-347.0	+10.5	-2.06	+84.0	+4.99	-1.70	-55.2	-2.51	+4.02
$R_{11}'=0$	+5.06	-1810.0	+25.0	-5.69	+444.2	+13.9	+0.27	-251.0	-7.36	+6.65
$R_{22}'=0$	+3.30	-67.1	+7.73	-1.37	+15.1	+3.28	-2.07	-17.8	-1.58	+3.51
$R_{12}=0$	+3.23	0.00	+7.06	-1.20	-1.46	+2.87	-2.16	-8.80	-1.36	+3.39
$R_{23}=0$	+3.24	-5.92	+7.12	-1.22	0.00	+2.91	-2.16	-9.59	-1.38	+3.40
Binary	+3.24	-----	-----	-1.22	-----	+2.91	-2.28	-----	-1.38	+3.52

Units of R_{ik} = Joule. cm. sec. mole^{-2}

TABLE 5.3

0.1 molar NaCl MOBILITY COEFFICIENTS

ASSUMPTION	ℓ_{11} x10^{13}	ℓ_{12} x10^{17}	ℓ_{22} x10^{16}	ℓ_{13} x10^{12}	ℓ_{23} x10^{15}	ℓ_{33} x10^{11}
$\ell_{23}=0$	3.66	3.02	1.40	1.53	0.00	4.07
$\ell_{13}/c_1=\ell_{23}/c_2$	3.66	3.38	1.44	1.53	2.19	4.21
$\ell_{12}=0$	3.66	0.00	1.10	1.51	-18.5	2.94
$R_{11}'=0$ and matrix	3.66	-1.81	0.92	1.50	-29.4	2.27
$R_{22}'=0$ and matrix	3.66	2.06	1.31	1.53	-5.91	3.71
$R_{12}=0$ and matrix	3.66	3.16	1.42	1.53	0.85	4.12
$R_{23}=0$ and matrix	3.66	3.06	1.40	1.53	0.13	4.08
Binary	3.66	----	----	1.53	----	4.07

Units of ℓ_{ik} = mole^2. Joule^{-1}. cm^{-1}sec^{-1}

are positive. (section 2.2.2)). Similarly $\ell_{23} = 0$ will give the 'wrong' sign for R_{23} and the 'correct' ones for R_{12} and R_{13}, while $R_{12} = 0$ (equivalent to the identity $\ell_{12}\ell_{33} = \ell_{13}\ell_{23}$) and $R_{23} = 0$ ($\ell_{11}\ell_{23} = \ell_{31}\ell_{12}$) automatically give the 'correct' signs for the other cross coefficients. It is clear then that setting coefficients to zero can have far reaching consequences. R_{13}, whose sign is determined by that of $\ell_{12}\ell_{23} - \ell_{13}\ell_{22}$, is not sensitive to ℓ_{12} or ℓ_{23} assumptions as the second term dominates by virtue of the relatively large ℓ_{13}. In general, assumptions involving the minor component, 2, do not affect the sign of the major coefficients and scarcely affect their magnitude.

5.2.1 0.1 Molar Sodium Chloride Results

The R and ℓ coefficients calculated for the membrane equilibrated in 0.1 molar sodium chloride are shown in Tables 5.2 and 5.3 respectively. From the discussion in section 5.1 it was suggested that the best assumptions were $R_{22}' = 0$ and $\ell_{23} = 0$, in that order. Agreement between the two approaches is good but, unexpectedly, the coefficients calculated from assumptions $R_{12} = 0$ and $R_{23} = 0$ also agree well. $R_{11}' = 0$ gives results at odds with all the other assumptions and even gives the major parameter R_{14} the 'wrong' sign. There can be little doubt that isotope-isotope interaction is not negligible for the counterion. Of the useful assumptions, $R_{22}' = 0$ and $\ell_{12} = 0$ do not put a sign restriction on ℓ_{23} and in these it is negative. ℓ_{23} is however the least well defined of all the ℓ coefficients, since it is calculated as the difference of two almost equal quantities. It would require a variation in t_3 of less than the experimental error of $\approx 1\%$ to change the sign. It is interesting that the assumption, $\ell_{12} = 0$ is the poorest

assumption after $R_{11}' = 0$. The cause of this lies in the relative magnitudes of ℓ_{12} and ℓ_{22} which appear together in the expression for t_2, equation 2.24b. Other assumptions indicate that ℓ_{12} is some 20% of ℓ_{22}, thus setting it to zero seriously underestimates ℓ_{22} and the effect compounds itself through the remainder of the calculations.

The frictional interactions of the ionic species with water measured by R_{13}, R_{23} and R_{34} are all of the same order of magnitude showing that the ion-water interaction is similar for all three. The tendency exhibited towards a negative ℓ_{23} manifests itself in the apparently 'wrong' sign for R_{23} but this is of little significance. While ion-dipole interactions are being discussed it is worth pointing out that the assumption $\ell_{13}/c_1 = \ell_{23}/c_2$ does give the plausible result that the sodium ion has a stronger coupling interaction than chloride with the water. The interaction of species 1 and 4 with water are identical within experimental error and may well reflect the fact that neither of these ions is capable of positively orientating water molecules (82). A further consequence of this equality is that $R_{11} = R_{44}$. This can be shown by expanding c_1R_{11} and c_4R_{44} according to equation 2.40 as

$$c_1R_{11} = - c_2R_{12} - c_3R_{13} - c_4R_{14} \qquad (5.7a)$$

$$c_4R_{44} = - c_1R_{14} - c_2R_{24} - c_3R_{34} \qquad (5.7b)$$

c_2R_{12} and c_2R_{24} are unimportant since c_2 is so small, and as c_1 and c_4 are virtually identical, the net result is the equality of R_{11} and R_{44}. The forms of equations 5.7 applicable to the binary approximation have a further use in that the breakdown of the c_iR_{ii} in terms of the percentage friction of species i with each of the other species present (except

TABLE 5.4

1.0 molar NaCl FRICTIONAL COEFFICIENTS

ASSUMPTION	R_{11} $_{-12}$ x10	R_{12} $_{-11}$ x10	R_{22} $_{-14}$ x10	R_{13} $_{-11}$ x10	R_{23} $_{-11}$ x10	R_{33} $_{-10}$ x10	R_{14} $_{-12}$ x10	R_{24} $_{-12}$ x10	R_{34} $_{-11}$ x10	R_{44} $_{-12}$ x10
$\ell_{23}=0$ and matrix inversion	+3.67	-10.8	+2.49	-1.74	+0.51	+4.97	-2.44	-8.77	-2.02	+4.42
$\ell_{13}/c_1=\ell_{23}/c_2$ and matrix	+3.63	+0.21	+2.14	-1.61	-3.50	+4.51	-2.54	-5.51	-1.65	+4.11
$\ell_{12}=0$ and matrix	+3.81	-57.0	+3.97	-2.27	+17.3	+6.89	-2.01	-22.5	-3.59	+5.69
$R_{11}'=0$	+4.92	-409.6	+15.2	-6.30	+145.8	+21.6	+1.28	-127.1	-15.6	+15.4
$R_{22}'=0$	+3.67	-11.5	+2.52	-1.75	+0.78	+5.00	-2.43	-9.00	-2.05	+4.44
$R_{12}=0$	+3.63	0.00	+2.15	-1.61	-3.42	+4.52	-2.54	-5.57	-1.66	+4.12
$R_{23}=0$	+3.66	-9.39	+2.45	-1.72	0.00	+4.91	-2.45	-8.36	-1.98	+4.38
Binary	+3.68	-----	-----	-1.74	-----	+4.97	-2.49	-----	-2.00	+4.11

TABLE 5.5

1.0 molar NaCl MOBILITY COEFFICIENTS

ASSUMPTION	$\ell_{11_{13}}$ x10	$\ell_{12_{15}}$ x10	$\ell_{22_{15}}$ x10	$\ell_{13_{12}}$ x10	$\ell_{23_{15}}$ x10	$\ell_{33_{11}}$ x10
$\ell_{23}=0$	3.27	1.18	4.02	1.14	0.00	2.41
$\ell_{13}/c_1=\ell_{23}/c_2$	3.28	1.90	4.74	1.19	43.5	2.67
$\ell_{12}=0$	3.26	0.00	2.83	1.07	-71.3	1.98
$R_{11}'=0$ and matrix	3.25	-0.96	1.87	1.01	-129.3	1.63
$R_{22}'=0$ and matrix	3.27	1.14	3.98	1.14	-2.24	2.40
$R_{12}=0$ and matrix	3.28	1.89	4.72	1.19	42.4	2.67
$R_{23}=0$ and matrix	3.27	1.25	4.09	1.15	4.40	2.44
Binary	3.26	----	----	1.14	----	2.41

TABLE 5.6

INTRINSIC MOBILITIES ℓ_{ii}/c_i

	0.1 M Na Cl	1.0 M Na Cl	0.1 M Na I
ℓ_{11}/c_1 ($\times 10^{10}$)	3.55	2.97	0.230
ℓ_{22}/c_2 ($\times 10^{10}$)	0.877	0.984	——
ℓ_{33}/c_3 ($\times 10^{10}$)	40.0	29.6	12.7

itself) can be studied. Consideration of this however will be deferred until the iodide results are discussed in section 5.2.3.

5.2.2 1.0 Molar Sodium Chloride Results

The 1.0 molar results are set out in Tables 5.4 and 5.5. It will be observed that all the major R coefficients have significantly increased in magnitude over their corresponding values in the 0.1 molar system. The primary cause is increased tortuosity in the more concentrated solution which enhances the influence of the matrix on the major species. The R_{2k} coefficients on the other hand are reduced showing the increased permeability of the coion at the higher external concentration as Donnan exclusion begins to break down. Similar trends are apparent in the ℓ coefficients where the major ℓ coefficients fall while the ℓ_{2k} rise. Intrinsic mobilities provide an alternative method of estimating the relative ease of movement of the mobile species. Defined as ℓ_{ii}/c_i (19), these measure the relative ease with which each species i can move under an applied force in the absence of interactions with other species. Table 5.6 gives the values of ℓ_{ii}/c_i for species 1, 2 and 3 at 0.1 and 1.0 molar external sodium chloride and shows that ℓ_{11}/c_1 and ℓ_{33}/c_3 decrease as expected. The near constancy of ℓ_{22}/c_2, however, implies that the coion finds it no more difficult to move in the more condensed system. In osmotic experiments it is observed that a relatively large flow of water is caused by a relatively small force. This observation appears again in a different form in Table 5.6 where it will be noted that the intrinsic mobility of water is much greater than either of the ions.

In the 1.0 molar system the coion is present to ≈ 4 per cent of the counterion and while the binary approximation is still useful, it is

apparent that some of the assumptions are reaching the limit of their applicability. As in the 0.1 molar system, the results obtained from $R_{11}' = 0$ differ considerably from all the others - which again indicates the importance of counterion isotope-isotope interaction. ℓ_{12} is now large enough to have some effect on ℓ_{11} and although ℓ_{22} has increased, the increase in ℓ_{12} is greater, making $\ell_{12} = 0$ an even poorer assumption than it was at 0.1 molar. There is again a tendency for ℓ_{23} to be negative, but from the earlier arguments of section 5.2.1, this cannot be considered to be significant. In both the 0.1 and 1.0 molar results ℓ_{33}, a major parameter, is subject to some variation in magnitude according to the method of calculation. This is a direct result of the osmotic flow equation (2.35) in which ℓ_{33} is obtained as the difference of two terms of similar magnitude. In this respect there is some similarity to the calculation of ℓ_{23}.

If attention is now directed towards the R coefficient Table 5.4 it will be seen that this time assumptions $R_{22}' = 0$ and $\ell_{23} = 0$ give practically identical results. The Staverman assumption, $R_{23} = 0$ also agrees closely but the Spiegler assumption, $R_{12} = 0$, is beginning to deviate. This tends to confirm that the ion-dipole interaction, R_{23}, is less important than the coion-counterion interaction coefficient, R_{12}, as might be expected on a priori grounds. Indeed where the two coefficients are calculated R_{12} tends to be the larger.

Much of the discussion of ion-water interactions in section 5.2.1 is again valid but this time the agreement in R_{13} and R_{34} (and consequently R_{11} and R_{44}) is not nearly so good. Again it would appear that the coion is present in sufficient quantity to affect significantly the

major parameters. An unusual feature of the results at both concentrations has been that R_{24} has remained a stable negative quantity regardless of the assumption employed. Moreover it is also reasonably large - contrary to expectation as species 2 and 4 having a repulsive interaction would lead to the prediction that they would occupy different regions of the exchanger as far as possible, with a consequent small, positive R_{24}. The equation from which R_{24} is calculated is

$$c_4R_{24} = -c_1R_{21} - c_2R_{22} - c_3R_{23} \qquad (5.8)$$

and if the terms on the right hand side are examined, it is observed that the large negative R_{24} is caused by the large, positive c_2R_{22}. If for the meantime Kedem's hypothesis about the signs of R coefficients is accepted and that R_{24} ought to be positive, then evidently c_2R_{22} is "too big" or to put it another way D_{22} is "too small". One possible explanation for this behaviour is that there is some form of ion pairing involving the sodium ions; perhaps of the form envisaged by Gustafson (69) occurring close to the polymer chains, or perhaps simply a result of the high internal molality of the exchanger phase. Gustafson - type ion pairing would also explain the odd trend of ℓ_{22}/c_2 as the proportion of coions ion-paired increases as the external concentration decreases according to this theory. The overall effect would therefore be a drop in intrinsic mobility as the external concentration decreased. The above postulate is tentative but does explain many of the features of the results as they relate to the coion. Further evidence may be obtained from the study of electron micrographs which comprises part of the next chapter.

CHLORIDE AND IODIDE R - AND ℓ - COEFFICIENTS
BINARY APPROXIMATION

TABLE 5.7

R - COEFFICIENTS

BINARY	$R_{11_{-12}}$ x10	$R_{13_{-11}}$ x10	$R_{33_{-10}}$ x10	$R_{14_{12}}$ x10	$R_{34_{-11}}$ x10	$R_{44_{-12}}$ x10
0.1 Molar Na I	+38.9	-3.76	+18.1	-37.5	-3.31	+38.8
0.1 Molar Na Cl	+3.24	-1.22	+2.91	-2.28	-1.38	+3.52
1.0 Molar Na Cl	+3.68	-1.74	+4.97	-2.49	-2.00	+4.11

TABLE 5.8

ℓ - COEFFICIENTS

BINARY	$\ell_{11_{13}}$ x10	$\ell_{13_{12}}$ x10	$\ell_{33_{11}}$ x10
0.1 Molar Na I	0.262	0.00545	0.564
0.1 Molar Na Cl	3.66	1.53	4.07
1.0 Molar Na Cl	3.26	1.14	2.41

5.2.3 0.1 Molar Sodium Iodide Results and Chloride/Iodide Comparisons

The 0.1 molar sodium iodide results are set out in Tables 5.7 and 5.8. The assumption made in these calculations is that the effect of species 2 on the major parameters is negligible and, as was discussed earlier, this is true even in the 1.0 molar results. As in the 0.1 molar sodium chloride results it will be observed that R_{13} and R_{34} (and hence R_{11} and R_{44}) are virtually identical showing that ionic species 1 and 4 interact similarly with water. It is interesting that even though the water content of the membrane in the iodide form is half of that in the corresponding chloride form, the ion-water frictional coefficients only rise by a factor of about 3 (and two-thirds of that increase may be ascribed to tortuosity). This would suggest that ion-water interactions are of secondary importance in this system otherwise the major reduction in water content ought to have brought about an increase in R_{13} and R_{34} as marked as that in the other R coefficients. It may well be that the counterions are located for most of the time close to the fixed charges and therefore, although the membrane shrinks, the counterions and fixed charges are in much the same environment. The value of R_{14} in the iodide results is unusually large and barely smaller than R_{11} and R_{44}. Equations 5.7, ignoring coion, may be written

$$c_1 R_{11} = -c_3 R_{13} - c_4 R_{14} \qquad (5.9a)$$

$$c_4 R_{44} = -c_1 R_{14} - c_3 R_{34} \qquad (5.9b)$$

and show that the near equality of R_{11} and R_{44} with R_{14} results from the dominance of the counterion-matrix frictional term on the right hand side. Equations 5.9 can be used further to calculate the percentage

TABLE 5.9

$c_i R_{ii}$ - ANALYSIS OF FRICTIONAL INTERACTIONS

	c_1R_{11} =	$-c_3R_{13}$	$-c_4R_{14}$
	AMF C-60	57.2%	42.8%
	AMF C-103	54.9%	45.1%
AMF A-104 This work	0.1M NaCl	32.3%	67.7%
"	1.0M NaCl	34.9%	65.1%
"	0.1M NaI	3.8%	96.2%
	c_3R_{33} =	$-c_1R_{31}$	$-c_4R_{34}$
	AMF C-60	56.3%	43.7%
	AMF C-103	59.2%	40.8%
AMF A-104 This work	0.1M NaCl	46.9%	53.1%
"	1.0M NaCl	47.5%	52.5%
"	0.1M NaI	53.2%	46.8%
	c_4R_{44} =	$-c_1R_{14}$	$-c_3R_{34}$
	AMF C-60	49.7%	50.3%
	AMF C-103	54.4%	45.6%
AMF A-104 This work	0.1M NaCl	65.0%	35.0%
"	1.0M NaCl	62.8%	37.2%
"	0.1M NaI	96.7%	3.3%

friction that any species has with any other species (excluding itself). Table 5.9 shows the analysis of the frictional interactions of species 1, 3 and 4 in all the systems studied, together with similar data calculated from published material on A.M.F. C-60 (79) and A.M.F. C-103 (28) cation exchange membranes.in the sodium form equilibrated with 0.1 molar sodium chloride. Both cation exchangers show a similar pattern of frictional interactions even although properties such as water content and capacity differ. Of special interest however is the polystyrenesulphonate-sodium interaction. Ion-matrix interactions of this type have been examined in p.m.r. and Raman spectroscopic studies (83)(84)(85)(86)(87)(88) and no indication of covalent character has been observed, although electrostatic binding to form ion pairs cannot be detected by these methods. More evidence comes from a study of Strauss and Leung (89) where volume changes accompanying interactions between various polyelectrolytes containing sulphonate, carboxylate, phosphonate or phosphate groups and a number of alkali and alkaline earth cations were measured. Of all the polyanions only polystyrene sulphonate did not show effects large enough to implicate site binding as the cause. This conclusion is supported by recent work of McHardy, Meares and Thain (65) on Zeo-karb 315 phenol sulphonic acid membranes where it is shown that variations in diffusion coefficients can be explained without recourse to ion pairing, nor is there any evidence of such found. It is not possible to dismiss completely any matrix-counterion association in the sodium polystyrene sulphonate system, but if it does exist, its effects appear to be minimal. The expansion of c_1R_{11} for the cation exchangers shows in fact that the

counterion has a greater frictional interaction with the water than with the matrix. For the anion exchanger however, the chloride counterion has twice as much friction with the matrix as with the water and the iodide form has practically all of its frictional interactions with the matrix. In the iodide form this means that the only species to exert appreciable influence on the movement of the counterion (apart from other counterions) is the matrix, and thus points very strongly towards a specific matrix-iodide interaction. A specific matrix-chloride interaction is less obvious and, in addition, the effects of the method of calculation cannot be ignored. Equation 5.9a measures the relative importance of 1-3 and 1-4 interactions. In the cation exchanger the 1-3 interaction is sodium-water and in the anion exchanger chloride-water. As the sodium ion has a stronger interaction than chloride with water (see for example Miller's sodium chloride data (19)), c_3R_{13} in the anion exchange system will contribute less than in the cation exchange system, so enhancing the relative contribution of c_4R_{14}. Another approach, free from these ambiguities, is however possible, that of coupling coefficients. These were originally defined for a two flow system by Kedem and Caplan (90) as

$$q = \ell_{12} / \sqrt{\ell_{11} \cdot \ell_{22}} = -R_{12} / \sqrt{R_{11} \cdot R_{22}} \qquad (5.10)$$

The calculations were later extended by Caplan (91)(92) to multiple flow systems where now

$$q^{\mp}_{ij} = \ell_{ij} / \sqrt{\ell_{ii} \cdot \ell_{jj}} \qquad (5.11)$$

$$q_{ij} = |R_{ij}| / \sqrt{R_{ii} \cdot R_{jj}} \qquad (5.12)$$

and there is no longer equality between $q^{\mp}_{ij}$ and q_{ij}. $|R_{ij}|$ is the modulus of R_{ij}.

TABLE 5.10

q_{ij} COUPLING COEFFICIENTS

		q_{13}	q_{14}	q_{34}
	AMF C-60	0.57	0.46	0.47
	AMF C-103	0.57	0.50	0.43
AMF A-104 This work	0.1M NaCl	0.40	0.68	0.43
"	1.0M NaCl	0.41	0.64	0.44
"	0.1M NaI	0.14	0.96	0.13

The importance of the coupling coefficient is that it provides a quantitative measure of the degree of coupling between the flows of species i and j. Thus if $q^{\mp}_{ij}$ or $q_{ij} = 0$ then a flow of i would have no effect on j and if $q^{\pm}_{ij}$ or $q_{ij} = 1$ then there would be complete coupling between flows of the two species. q^{*}_{ij} or q_{ij} cannot be greater than unity as this would constitute a violation of the O.R.R. As discussed in section 2.2.2, equation 5.11 is intrinsically unsatisfactory since the values of any ℓ coefficients are dependent on the frame of reference chosen, and contain an unknown contribution from that source. R coefficients, on the other hand are uniquely specified and so consequently are the q_{ij} of equation 5.12. The values of q_{13}, q_{14} and q_{34} calculated from the same data used to calculate the percentage frictions are shown in Table 5.10. The matrix-counterion coupling coefficient, q_{14}, is significantly higher for quaternary ammonium-chloride than for polystyrene sulphonate-sodium, which suggests that there may well be a specific quaternary ammonium - chloride interaction. This would appear to be the best indication of the relative importance of quaternary ammonium-chloride ion association which is likely to be forthcoming from this study of transport properties.

The analysis of c_4R_{44} is similar to that of c_1R_{11}, but that of c_3R_{33} is of interest showing that in all five cases the friction of the water with the other mobile species is divided almost evenly between counterion and matrix-fixed charge. This is especially so in the anion exchanger although probably not independent of ion association in this system. As would be expected there is a tendency for the sodium-water interaction

TABLE 5.11

ISOTOPE-ISOTOPE INTERACTIONS - WATER

EXT. CONCN.	$R_{33}{}_{-11}$ x10	$R_{33}-R_{33}'{}_{-11}$ x10	$R_{33}'{}_{-11}$ x10	$R_{33}-R_{33}'/R_{33}$	R_{33}'/R_{33}
0.1M NaCl	0.333	1.14	-0.81	3.44	-2.44
1.0M NaCl	0.500	1.89	-1.4	3.78	-2.78
0.1M NaI	1.81	6.60	-4.8	3.65	-2.65

TABLE 5.12

ISOTOPE-ISOTOPE INTERACTIONS - COUNTERION

EXT. CONCN.	$R_{11}{}_{-12}$ x10	$R_{11}-R_{11}'{}_{-12}$ x10	$R_{11}'{}_{-12}$ x10	$R_{11}-R_{11}'/R_{11}$	R_{11}'/R_{11}
0.1M NaCl	3.31	5.05	-1.74	1.52	-0.52
1.0M NaCl	3.67	4.92	-1.25	1.34	-0.34
0.1M NaI	38.9	83.7	-44.8	2.15	-1.15
AMF C-60	1.01	1.43	-0.43	1.42	-0.42
AMF C-103	2.81	3.25	-0.44	1.16	-0.16

to be greater than the sulphonate-water interaction in the cation exchanger and this is also reflected in q_{13} and q_{34}.

5.3 Isotope-Isotope Interaction

With the complete set of phenomenological coefficients calculated, isotope-isotope interactions can be examined more closely. The starting point is equation 5.1, $D_{ii} = \frac{RT}{c_i(R_{ii}-R_{ii}')}$, where D_{ii} is the self diffusion coefficient of species i in the membrane. Coion isotope-isotope interaction has already been discussed in section 5.1.1 and the results confirm that R_{22}' is negligible in comparison to R_{22}. The most interesting interactions are however R_{11}' and R_{33}'. It was argued on a priori grounds that R_{11}' should be a significant fraction of R_{11}, a proposition which was supported by the very poor agreement between coefficients calculated on the assumption $R_{11}' = 0$ with other assumptions. The results of isotope-isotope interaction calculations are set out in Tables 5.11 and 5.12 where R_{33}' is seen to be large compared to R_{33} and also negative. The ratio R_{33}'/R_{33} is the same within experimental error for the three systems studied and would indicate that the interactions of the membrane water with all other species do not alter significantly from the chloride to the iodide form. Considering the large differences in transport properties between these two forms, this is an unexpected result.

The negative sign of R_{33}' is as would be predicted by the Kedem approach (25)(29) since water has an attractive interaction with itself. The ratio $R_{33}-R_{33}'/R_{33}$ is not numerically large as the contributions of water interactions with all other species have become significant. The kind of variations in the ratio obtained in practice are brought out very clearly

TABLE 5.13

CALCULATION OF R_{11}' AND R_{22}' IN AQUEOUS SODIUM CHLORIDE

(FROM J.H. WANG (66)(67) AND D.G. MILLER (19))

MOLARITY	R_{22} x10^{-11}	R_{11} x10^{-11}	$R_{22}-R_{22}'$ x10^{-11}	$R_{11}-R_{11}'$ x10^{-11}	R_{22}' x10^{-11}	R_{11}' x10^{-11}
0.01	191.8	125.6	189.2	---	2.6	---
0.05	39.69	25.46	38.14	25.3	1.54	0.66
0.10	20.28	13.26	18.9	12.78	1.30	0.48
0.50	4.430	2.870	3.76	2.67	0.67	0.19
1.0	2.388	1.532	1.98	1.40	0.41	0.13
2.0	1.361	0.859	1.10	0.777	0.261	0.082
3.0	1.032	0.644	0.810	0.573	0.222	0.071

in data assembled by Paterson (27). Starting with pure water where $R_{33}=0$ and $R_{33}-R_{33}'/R_{33}$ is therefore infinity, he looks at this ratio in a series of membranes in which the water content falls and the interactions of water with all other species increase. $R_{33}-R_{33}'/R_{33}$ falls from about 5×10^6 in microporous Millipore membranes where R_{33} is relatively small to about 10 in commercial cation exchange membranes. The anion exchanger studied in this work has a very low water content and the ratio falls to about 3.5. Values of near unity have been obtained in a biological membrane (93).implying a very low membrane water content or a very large degree of coupling between water and the other membrane species, or perhaps a combination of both effects. Perhaps the most interesting interaction of all is R_{11}' because here theoretical problems are encountered. The results show that R_{11}' is a significant fraction of R_{11} and, in fact, for the 0.1 molar sodium iodide system, is larger than R_{11}. The dangers in using D_{11} as a direct measure of R_{11} are obvious. The anomaly however lies not in the magnitude of R_{11}', striking though it is, but in the sign. Again applying the Kedem rule (25), R_{11}' ought to be positive as counterion-counterion interactions are repulsive, but in the three membrane systems for which results are available, R_{11}' is negative. This would seem to be more than a coincidence and it must be concluded that the effect is real. Table 5.13 shows R_{11}' and R_{22}' for the self diffusion of sodium and chloride ions over a range of concentrations in aqueous sodium chloride from the data of Wang (66)(67) and Miller (19). At all concentrations R_{11}' and R_{22}' remain positive. In the face of these seemingly paradoxical results the best course would appear to be a reconsideration of what is meant by isotope-isotope interaction. As

defined the term $c_i R_{ii'}$ measures the friction of one mole of i' with i which is at the concentration existing in the exchanger. The interpretation of the term can however be extended. $c_{i'} R_{i'i}$ similarly measures the friction of one mole of i with i' at the concentration existing in the exchanger. Therefore $c_i R_{ii'} + c_{i'} R_{i'i}$ sums all interactions of i molecules with i molecules, whether isotope or not. However by the O.R.R., $R_{ii'} = R_{i'i}$ and at tracer level $c_i \gg c_{i'}$ and so $c_i R_{ii'}$ approximates very closely to a measurement of the relative importance of all i - i kinetic interactions (compared to those of i with other species) in determining the behaviour of i in the membrane phase. For a sample of pure water, $R_{33} = 0$, and so $R_{33'}$ must be negative to give a positive D_{33}. Equally if species 2,3 and 4 could be removed from the ion exchange system - leaving a plasma of counterions - then again one would expect diffusion to occur normally and $R_{11'}$ would become negative by mathematical necessity. In such a situation all counterion kinetic interactions would be with other counterions. In an ion exchanger species 1 tends to be localised near the polymer chains, so with little coion present it would not be surprising therefore if a large number of counterion-counterion interactions occurred thus approaching the 'plasma' state. An important factor in determining the overall behaviour of species 1 would be its kinetic interactions with other counterions, which could be sufficient to make $R_{11'}$ negative. It is interesting to observe in support that the largest negative value of $R_{11'}$ occurs in the system with the highest counterion concentration. In solution, a binary electrolyte ion 1 is an average surrounded by ions of opposite charge and water, making 1-1 kinetic interactions relatively infrequent and

TABLE 5.14

CALCULATION OF L-COEFFICIENTS

0.1 Molar NaCl (Spiegler $R_{22}' = 0$ coefficients)

ℓ_{11}	$= 3.66_{10}^{-13}$	L_{11}	$= 4.86_{10}^{-13}$
ℓ_{12}	$= 1.94_{10}^{-17}$	L_{12}	$= 1.18_{10}^{-15}$
ℓ_{22}	$= 1.29_{10}^{-16}$	L_{22}	$= 1.32_{10}^{-16}$
ℓ_{13}	$= 1.52_{10}^{-12}$	L_{14}	$= 2.90_{10}^{-13}$
ℓ_{23}	$= -6.62_{10}^{-15}$	L_{24}	$= 1.40_{10}^{-15}$
ℓ_{33}	$= 3.67_{10}^{-11}$	L_{44}	$= 4.61_{10}^{-13}$

1.0 Molar NaCl (Spiegler $R_{22}' = 0$ coefficients)

ℓ_{11}	$= 3.27_{10}^{-13}$	L_{11}	$= 4.58_{10}^{-13}$
ℓ_{12}	$= 1.14_{10}^{-15}$	L_{12}	$= 1.20_{10}^{-14}$
ℓ_{22}	$= 3.97_{10}^{-15}$	L_{22}	$= 4.59_{10}^{-15}$
ℓ_{13}	$= 1.14_{10}^{-12}$	L_{14}	$= 2.75_{10}^{-13}$
ℓ_{23}	$= -2.58_{10}^{-15}$	L_{24}	$= 1.59_{10}^{-14}$
ℓ_{33}	$= 2.40_{10}^{-11}$	L_{44}	$= 4.08_{10}^{-13}$

unimportant. This should be especially so at low concentration and it is seen in Table 5.13 that R_{11}' and R_{22}' in sodium chloride solutions are at their largest positive values in dilute solutions and steadily decrease as the solution concentration increases. Further experiments on a wide variety of membranes would be necessary to confirm this hypothesis. It would be expected that as the exchanger phase becomes more and more like a normal solution with decreasing fixed charge concentration and increasing coion uptake, R_{11}' would change sign from negative to positive.

5.4 Membrane and Solvent Fixed Mobility Coefficients

To illustrate the drastic effect of changing the reference frame of mobility coefficients, the ℓ coefficients obtained from the assumption $R_{22}' = 0$ have been transformed into solvent-fixed L coefficients as in Appendix A.1. These are shown for the sodium chloride results at 0.1 and 1.0 molar in Table 5.14. Of the three coefficients defined in both frames of reference, (11,12,22) only the 22 coefficient remains relatively unchanged. This is a consequence implicit in Spiegler's assumption $R_{22}' = 0$ as the neglect of isotope-isotope interaction for coion means that ℓ_{22}' and L_{22}' are likewise zero. The coion self diffusion coefficient is independent of the frame of reference chosen and therefore with $\ell_{22}' = L_{22}' = 0$

$$D_{22} = RT. \frac{\ell_{22}}{c_2} = RT. \frac{L_{22}}{c_2} \qquad (5.13)$$

i.e. $\ell_{22} = L_{22}$ (5.14)

Equation 5.14 has interesting consequences. From equation A.1.6,

$$L_{22} = \ell_{22} - 2\frac{c_2}{c_3}\ell_{23} + \frac{c_2^2}{c_3^2}\ell_{33} \qquad (A.1.6)$$

In combination with equation 5.14 in immediately follows that

$$\ell_{23}/\ell_{33} = c_2/2c_3 \qquad (5.15)$$

ℓ_{33}, c_2 and c_3 are all positive terms so that ℓ_{23} must also be positive. The results suggested however that ℓ_{23} was negative, but again, as already argued, ℓ_{23} is the least well defined ℓ coefficient from an experimental viewpoint. Table 5.14 shows that ℓ_{22} and L_{22} are not identical but the agreement is more than satisfactory. For both sets L_{11} is about 50% larger than ℓ_{11} while L_{12} is some ten times larger than ℓ_{12} at 1.0 molar and almost one hundred times larger at 0.1 molar. q^*_{12} calculated from L coefficients is thus approximately seven and seventy times larger than the comparable quantity calculated from ℓ coefficients, which goes to prove that interpretation based on mobility coefficients must proceed with care.

L_{24} is positive whereas in ternary mixtures of electrolytes (the solution analogue), Miller (80) finds the equivalent coefficient to be negative. The positive sign of L_{24} in the 1.0 molar results is not a consequence of the negative sign of ℓ_{23} as it is in the 0.1 molar case, ($L_{24} = \frac{c_2 c_4}{c_3^2}\ell_{33} - \frac{c_4}{c_3}\ell_{23}$ (A.1.8)), but rather is caused by the dominance of the positive ℓ_{33} term in the above equation.

To make further use of the solvent fixed coefficients it would have been interesting to compare the tortuosity scaled coefficients with those of a suitable salt at the same concentration, as has been done with considerable success by Gardner and Paterson (79). However there are

TABLE 5.15

NERNST-PLANCK CALCULATIONS

0.1 M Na Cl N:P.	3.48_{10}^{-3}	-4.09	1.01001	-3.17_{10}^{-4}
Exp.	3.41_{10}^{-3}	-4.18	0.9997	$+3.00_{10}^{-4}$
0.5 M Na Cl N:P.	3.83_{10}^{-3}	-----	-----	-----
Exp.	-----	-3.84	0.997	3.42_{10}^{-3}
1.0 M Na Cl N:P.	3.53_{10}^{-3}	-2.83	1.0891	-5.20_{10}^{-3}
Exp.	3.06_{10}^{-3}	-3.48	0.991	$+8.62_{10}^{-3}$
2.0 M Na Cl N:P.	3.30_{10}^{-3}	-----	-----	-----
Exp.	-----	-3.07	0.975	2.48_{10}^{-2}
0.1 M Na I N:P.	2.37_{10}^{-4}	-2.12	0.9904	-3.04_{10}^{-4}
Exp.	2.42_{10}^{-4}	-2.08	1.0	1.0_{10}^{-4}

no solution coefficients available at such high concentrations as exist in the membrane phase. Even for such common salts as sodium and potassium chloride, phenomenological coefficients have only been obtained up to 3.0 molar.

5.5. Nernst-Planck Calculations

As discussed in Chapter 2 the Nernst-Planck flux equations can be used predictively. With diffusion and conductivity data, the water transference number, t_3 is given by

$$t_3 = \left(\frac{F^2}{RT\bar{k}} \left(\sum_i c_i D_{ii} z_i^2 \right) - 1 \right) \cdot \frac{c_3}{c_4 z_4} \qquad (2.71)$$

Diffusion and water transference data can be used to obtain the specific conductivity $\bar{k}$

$$\bar{k} = \frac{F^2}{RT} \left(\frac{\sum_i z_i^2 c_i D_{ii}}{\left(1 + \frac{c_4 z_4 t_3}{c_3} \right)} \right) \qquad (2.70)$$

and the transport numbers of the ions may be derived from conductivity, diffusion and water transference data.

$$t_i = \frac{F^2}{RT\bar{k}} \left(z_i^2 c_i D_{ii} + \frac{c_i z_i t_3}{c_3} \right) \qquad (2.72)$$

It is possible to obtain a prediction of $\bar{k}$ at all the concentrations studied, but the lack of an experimental $\bar{k}$ at 0.5 and 2.0 molar sodium chloride prevents an estimate of t_1, t_2 and t_3 at these concentrations, even though experimental values of these quantities have been obtained. The results of the calculations are summarised in Table 5.15. As

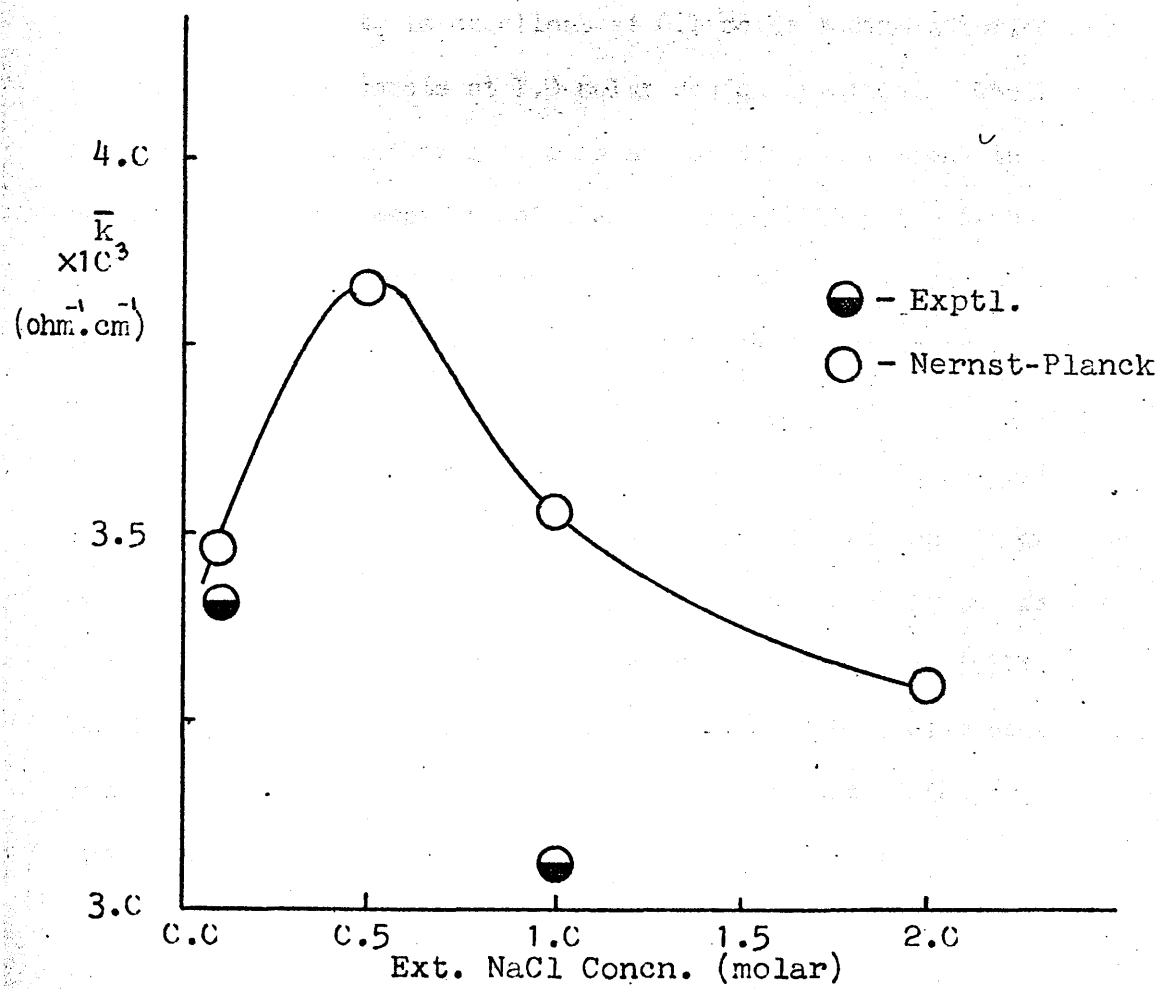


Fig. 5.1 Predicted and experimental specific conductivities

c_1D_{11} is much greater than c_2D_{22}, the Nernst-Planck $\bar{k}$ in the sodium chloride results follows the trend of D_{11}, and shows a maximum in the region of 0.5 molar. Where a comparison with experimental data is possible, agreement is good, and it is likely that the calculated $\bar{k}$, which is graphed in figure 5.1, would not be far from the experimental reality. The prediction of t_3 is excellent at 0.1 molar sodium chloride and iodide but only moderate at 1.0 molar sodium chloride. Whether this is merely an artefact or a consequence of the assumptions in the Nernst-Planck treatment is not clear. Nonetheless the Nernst-Planck flux equations do provide useful estimates of $\bar{k}$ and t_3, showing how well the explicit and implicit compensations discussed in Section 2.4 work. The same, unfortunately, cannot be said for t_1 and t_2, where the limitations of the Nernst-Planck approach are plain to see with $t_1 > 1$ and $t_2 < 0$. In fairness to the Nernst-Planck equations it must be pointed out that the system under study in this work is not favourable for this approach. The best results for t_1 and t_2, as implied in Section 2.4, would be obtained in a membrane of high water content and low internal molality where the effects of the neglect of isotope-isotope interactions and some cross coefficients would be less serious.

CHAPTER 6

MEMBRANE STRUCTURE FROM COION UPTAKE AND ELECTRON MICROGRAPHS

For a homogeneous ion exchange resin in equilibrium with an external 1:1 electrolyte of molality m, the Donnan expression, which governs the sorption of electrolyte by the resin, may be written

$$\bar{m}\,(M + \bar{m})\overline{\gamma_{\pm}} = m^2\gamma_{\pm} \qquad (6.1)$$

where $\bar{m}$ is the molality of the sorbed electrolyte, M is the molality of fixed groups, m is the external solution molality and $\gamma_{\pm}$, $\overline{\gamma}_{\pm}$ are the mean molal activity coefficients in the solution and resin respectively.

Since the first experimental investigation of electrolyte uptake in ion exchange resins in 1947 by Bauman and Eichhorn (94) the subject has been the source of considerable controversy. In contrast to the normal aqueous solution behaviour of strong electrolytes where the activity coefficients tend towards unity at infinite dilution, the resin activity coefficients fall to very low values (69)(95)(96)(97)(98)(99)(100)(101)(102)(103), meaning that the resin retains a good deal more electrolyte than would be predicted by the application of equation 4.1. Various explanations have been proposed such as heterogeneity (94)(97), mosaic behaviour (100)(104) and experimental error (104) - the basic philosophy being that once these effects were taken into account, the uptake would obey the homogeneous gel model implied by equation 6.1. None proved entirely satisfactory. The possibility that the low activity coefficients were a real

rather than an apparent effect was suggested by Gustafson (69) who pointed to a similar phenomenon in polyelectrolyte solutions (105)(106)(107)(108).

He considered that at low salt uptake values the activity of the coion is low owing to coion-counterion ion pairing close to the polymer chains, while the counterion activity remains virtually constant. The electrolyte sorption results presented by Gustafson in support of his hypothesis have been criticised as simply showing evidence of heterogeneity (109), but while accepting the criticism and applying suitable corrections, Gustafson has subsequently maintained his position (70). Other attempts to explain the low activity coefficients as a genuine effect have been based on the properties of electrical double layers (110)(111) and charged microcapillaries (112)(113). The opposite approach has been taken by Glueckauf and co-workers (37)(52)(68) who regard the effect solely as a consequence of the overall inhomogeneity of ion exchange resins, since at low external electrolyte concentration the major contribution to the observed electrolyte uptake will be from areas which have lower than average fixed charged densities (but which still obey equation 6.1). This view of ion exchange resins as being fundamentally inhomogeneous receives direct support from the available electron micrographs (52) (54)(114)(115)(116)(117)(118)(119)(120)(121) on ion exchange membranes. The theory developed by Glueckauf permits the calculation of the fractional site distribution in the exchanger from the electrolyte uptake data and the molality of the 'most continuous region' from uptake and coion permeability data, thus achieving a degree of structural analysis.

TABLE 6.1

COION UPTAKE DATA

C	m	$\bar{m}$	M	M+$\bar{m}$	$\gamma_{\pm}$	$\bar{\gamma}$ (from eq.6.1)
0.1 M NaCl	0.1005	0.0089	6.232	6.241	0.778	0.141
0.5 M NaCl	0.5062	0.0845	6.786	6.871	0.681	0.300
1.0 M NaCl	1.0222	0.2763	7.251	7.528	0.657	0.330
2.0 M NaCl	2.0859	0.6893	7.806	8.495	0.670	0.498
0.1 M NaI	0.1	0.0165	14.19	14.20	0.797	0.048

The experimental data obtained in this study, presented in Table 6.1, do not justify a serious investigation of electrolyte uptake as such, being limited in both scope and accuracy, but the chloride data in conjunction with the water contents does allow a Glueckauf type of structural analysis. For this reason the Glueckauf theory (52)(68) alone will be considered in more detail. Before proceeding to it, however, it will be observed that the mean molal activity coefficients in the membrane as calculated from equation 6.1 show the tendency to fall with decreasing external concentration as found by so many others. However, although the external salt concentrations remain relatively high the membrane activity coefficients are surprisingly small particularly in the iodide form. This cannot be ascribed to the experimental technique employed as dipping the membrane into an inactive solution would, if anything, remove too much isotope. The evidence again implicates quaternary ammonium-halide interactions as an important factor.

6.1 Structural Analysis by the Glueckauf Method - Fractional Site Distribution

The basic assumption of the Glueckauf approach is that the Donnan expression is valid for any small volume element of the exchanger. If the external solution molality is m (for simplicity assumed to be a 1:1 strong electrolyte) and the time averaged local fixed ion molality in the exchanger is M then the electrolyte uptake in this volume element $\bar{m}$ is given by solving the quadratic

$$\bar{m}\,(M + \bar{m})\,\bar{\gamma}_{\pm} = \alpha m^2 \gamma_{\pm} \qquad (6.2)$$

where α takes in the relatively invariant swelling pressure contribution

(which was implicitly included in the $\bar{\gamma}_{\pm}$ of equation 6.1). The further assumption is then made that $\bar{\gamma}_{\pm}$ is approximately proportional to $\gamma_{\pm}$, as the regions with $M + \bar{m} \gg m$, which would be expected to have values of $\bar{\gamma}_{\pm}$ greatly different from $\gamma_{\pm}$, will contribute only minutely to the average electrolyte uptake $\tilde{\bar{m}}$. The activity coefficients can thus be cancelled from equation 6.2 leaving a small factor which may be absorbed into α so that equation 6.2 can be rewritten

$$\left(\frac{\bar{m}}{\alpha m}\right)\left(\frac{M}{\alpha m} + \frac{\bar{m}}{\alpha m}\right) = 1 \qquad (6.3)$$

or in general

$$\frac{\bar{m}}{\alpha m} = f\left(\frac{M}{\alpha m}\right) \qquad (6.4)$$

At this stage a function ϕ is introduced such that the volume fraction, $d\phi$, of the exchanger has a fixed ion concentration between M and $M + dM$ i.e.

$$d\phi/dM = F(M) \qquad (6.5)$$

where $M = A$ when $\phi = 0$ and $M = B$ when $\phi = 1$ (since M must have lower and upper limits imposed by the system) and F(M) is a continuous function of M. Therefore

$$\int_{M=A}^{M=B} d\phi = 1 \qquad (6.6)$$

Two further definitions are now possible

$$\tilde{M} = \int_{M=A}^{M=B} M\,d\phi \qquad (6.7)$$

where $\tilde{M}$ is the mean molality of the fixed groups and

$$\tilde{\bar{m}} = \int_{\phi=0}^{\phi=1} \bar{m} d\phi \qquad (6.8)$$

In principle, the distribution function F(M) can be obtained from the experimental curve of uptake versus external concentration of electrolyte but experimental errors make this difficult. Glueckauf proposed the function

$$d\phi/dM = KoM^{-Z} \qquad (6.9)$$

where Z is a constant.

Substitution of equation 6.9 into equations 6.6 and 6.7 and integrating gives

$$Ko = (1-Z)/(B^{1-Z} - A^{1-Z}) \qquad (6.10)$$

and

$$Ko = \tilde{m}(2-Z)/(B^{2-Z} - A^{2-Z}) \qquad (6.11)$$

For most practical purposes the A terms may be neglected and equations 6.10 and 6.11 therefore define Ko and B as

$$Ko = (1-Z)^{2-Z}/((2-Z) \times \tilde{M})^{1-Z} \qquad (6.12)$$

$$B = (2-Z)x\tilde{M}/(1-Z) \qquad (6.13)$$

Substitution for $d\phi$ from equation 6.9 and $\bar{m}$ from equation 6.4 gives for $\tilde{\bar{m}}$,

$$\tilde{\bar{m}} = Ko(\alpha m) \int_{M=A}^{M=B} M^{-Z} . f\left(\frac{M}{\alpha m}\right) dM \qquad (6.14)$$

If now $y = M/\alpha m$ the equation may be rewritten

$$\tilde{\bar{m}} = Ko(\alpha m)^{2-Z} \int_{yA}^{yB} y^{-Z} f(y) dy \qquad (6.15)$$

where yA and yB are the values of y at M=A and M=B respectively. For a tight membrane the volume fraction ϕ is insignificant for values of M near zero and the uptake $\bar{m}$ is insignificant at high

values of M so the integral $\int_{yA}^{yB} y^{-Z} f(y)dy$ differs little from $I_o^{\infty} = \int_o^{\infty} y^{-Z} f(y)dy$ and the latter may be employed with equation 6.15 to give for α.

$$\alpha = \frac{1}{m}\left(\frac{\tilde{\bar{m}}}{K_o I_o^{\infty}}\right)^{\frac{1}{2-Z}} \qquad (6.16)$$

Equation 6.16 may also be written in the form

$$\tilde{\bar{m}}/m = \text{constant} \times m^{1-Z} \qquad (6.17)$$

which is the Donnan expression with the assumption

$$\tilde{M} + \tilde{\bar{m}} \approx \tilde{M} \approx \text{constant} \qquad (6.18)$$

A plot of log $(\tilde{\bar{m}}/m)$ versus log m should therefore give a straight line of gradient (1-Z).

The expression 6.18 is only a good approximation if there is little change in the swelling and the uptake is small compared to $\tilde{M}$ - not the case for a highly swollen exchanger in medium to high concentrations of external electrolyte, and in these circumstances equation 6.17 is inadequate. Glueckauf's own data (37) shows deviations at the high end of the concentration range from these effects but, as he is mainly concerned with uptakes in the range of validity of equation 6.17, they are not important. In this work changes in $\tilde{M}$ and $\tilde{\bar{m}}$ caused by swelling changes and increasingly important uptake contributions cannot be ignored, as Table 6.1 shows, and the full Donnan type expression

$$\frac{\tilde{\bar{m}}}{m} = \text{constant} \times \left(\frac{m}{\tilde{M} + \tilde{\bar{m}}}\right)^{1-Z} \qquad (6.19)$$

was used instead, so that a plot of log $\left(\frac{\tilde{\bar{m}}}{m}\right)$ versus log $\left(\frac{m}{\tilde{M} + \tilde{\bar{m}}}\right)$ gives a straight line of gradient 1-Z. The physical significance of

TABLE 6.2

GLUECKAUF PARAMETERS - SODIUM CHLORIDE DATA

EXTERNAL CONCENTRATION	Z	Ko	B	α
0.1 M	0.50	0.116	18.70	0.78
0.5 M	0.50	0.111	20.36	0.72
1.0 M	0.50	0.107	21.75	0.80
2.0 M	0.50	0.103	23.42	0.74

TABLE 6.3

FRACTIONAL SITE DISTRIBUTION

Range in M	EXTERNAL CONCENTRATION 0.1 M NaCl $\Delta\phi$ (%)	2.0 M NaCl $\Delta\phi$ (%)
B - 15.0	13.4	23.1
15.0 - 10.0	16.5	14.7
10.0 - 5.0	21.5	19.0
5.0 - 1.0	28.7	25.5
1.0 - 10^{-1}	13.6	12.1
10^{-1} - 10^{-2}	4.31	3.83
10^{-2} - 10^{-3}	1.36	1.21
10^{-3} - 10^{-4}	0.43	0.38
10^{-4} - 10^{-5}	0.13	0.12
$< 10^{-5}$	0.07	0.06

Z in the Glueckauf approach is that it provides a measure of the heterogeneity of the system. A value of Z = 0 means that the system follows the classical Donnan expression and is thus perfectly homogeneous. As the heterogeneity of the system increases so also does the value of Z. The value of Z obtained in this work, 0.50, is similar to those reported for other ion exchangers by Glueckauf (52)(68), and Arnold (122). One relevant feature is the disagreement between Glueckauf's Z value for his AMF A-104 membranes, 0.76, and that of 0.50 obtained here. As has been seen throughout the two samples of AMF A-104 membranes appear to have quite different properties. Given a value of Z, values of Ko, B and α were calculated for each concentration studied using equations 6.12, 6.13 and 6.16 respectively and these are shown in Table 6.2. The Runge-Kutta method was used to solve equation 6.9 for values of ϕ at given values of M and a fractional site distribution was built up for each separate M. These are shown for the 0.1 and 2.0 molar cases in Table 6.3. A large fraction of volume elements have values of M not too different from $\tilde{M}$ as might be expected and, as befits a 'tight' membrane, only a very small fraction of volume elements have low values of M. In 2.0 molar sodium chloride the membrane contains considerably less water than at 0.1 molar and consequently $\tilde{M}$ at 2.0 molar is higher than the value at 0.1 molar and the fractional site distribution shifts to higher values of M.

6.2 Electron Micrographs

To obtain evidence of heterogeneity implied by the Glueckauf approach a less equivocal method is required. Optical microscopy is possible but electron microscopy is preferable as this technique allows

FIGURE 6.1

ELECTRON MICROGRAPH OF A SECTION OF A.M.F. A-104 MEMBRANE IN THE CHROMATE FORM.

MAGNIFICATION X 170,000.

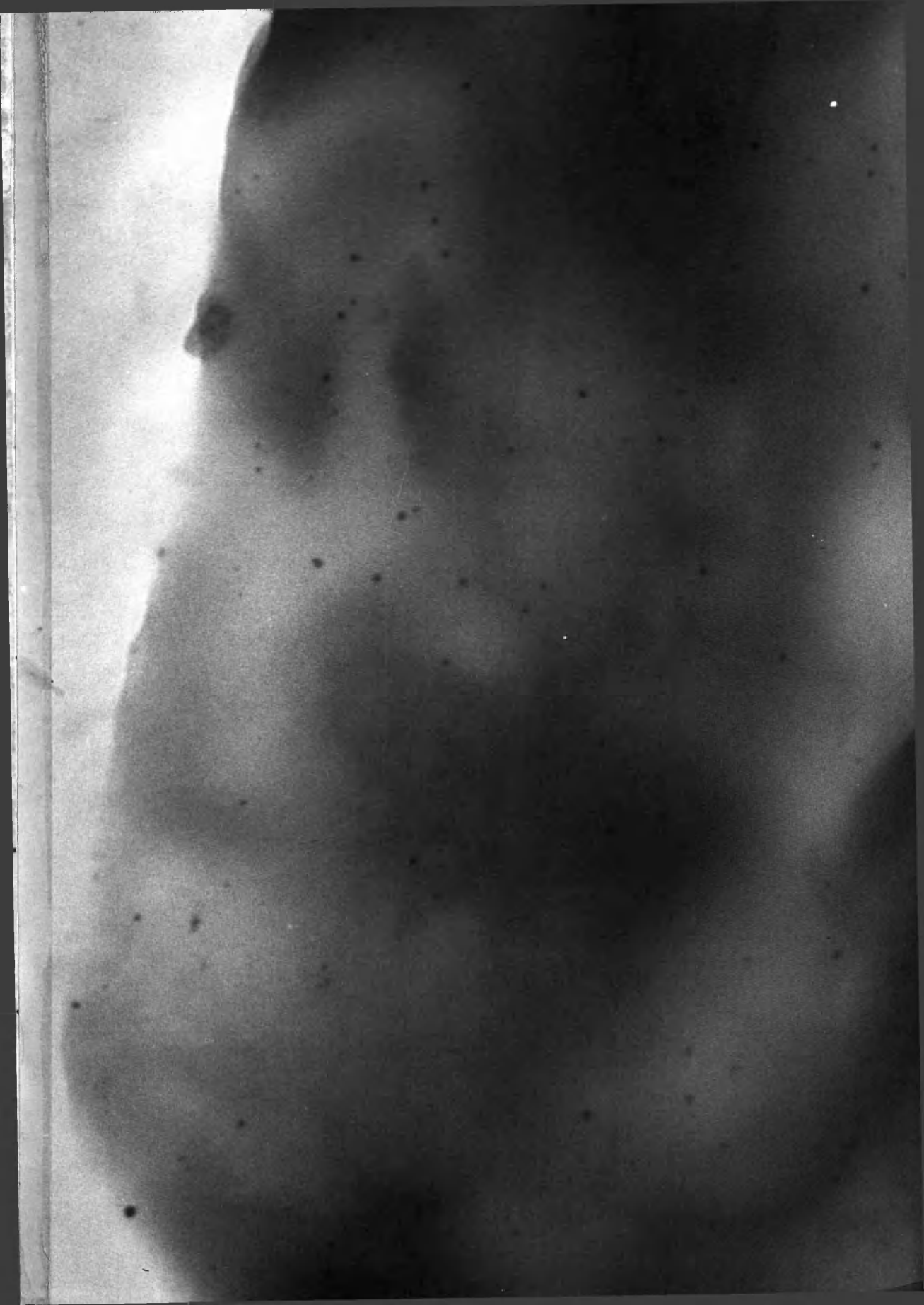


FIGURE 6.2

ELECTRON MICROGRAPH OF A SECTION OF A.M.F. A-104 MEMBRANE IN THE CHROMATE FORM.

MAGNIFICATION X 170,000.

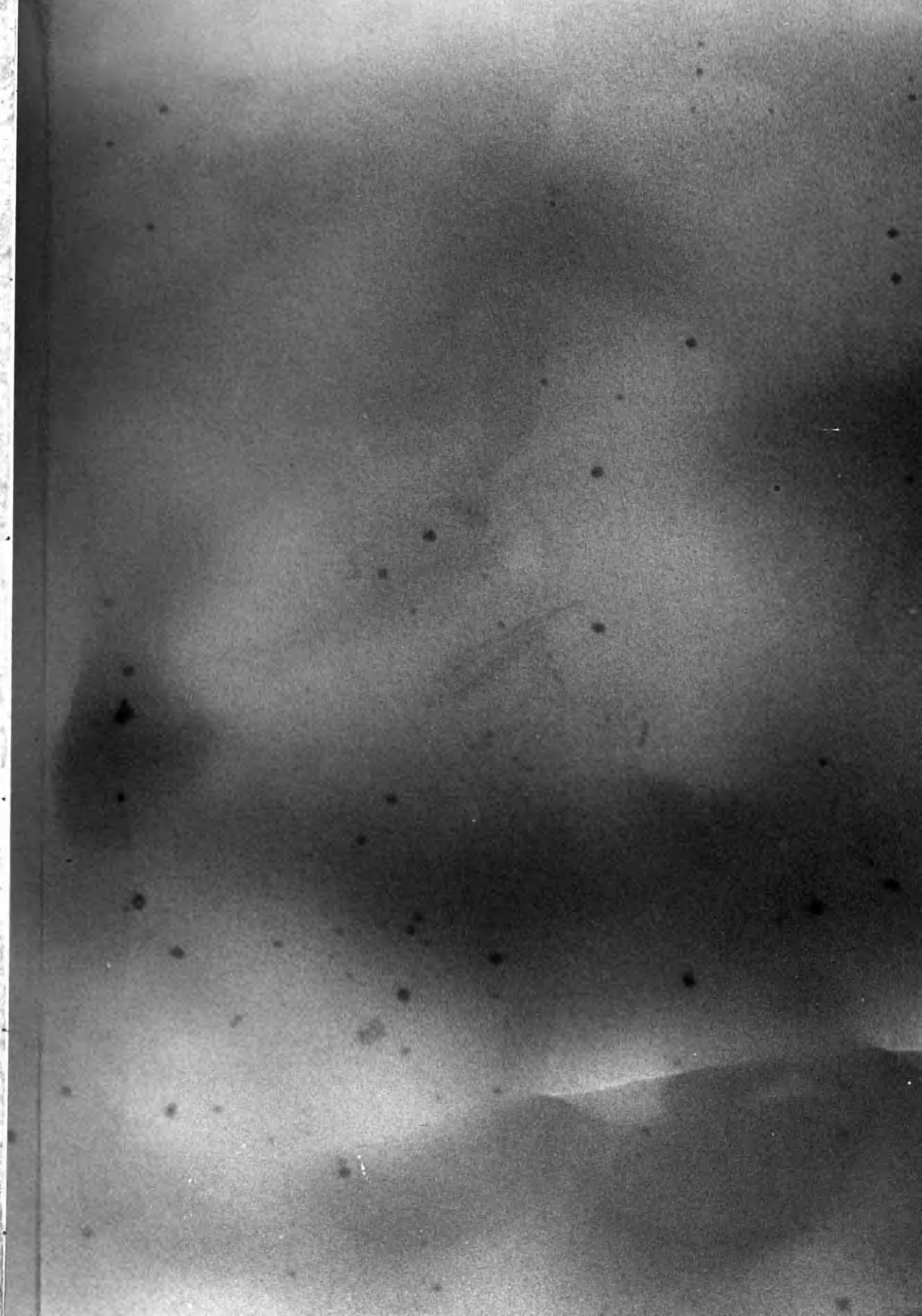
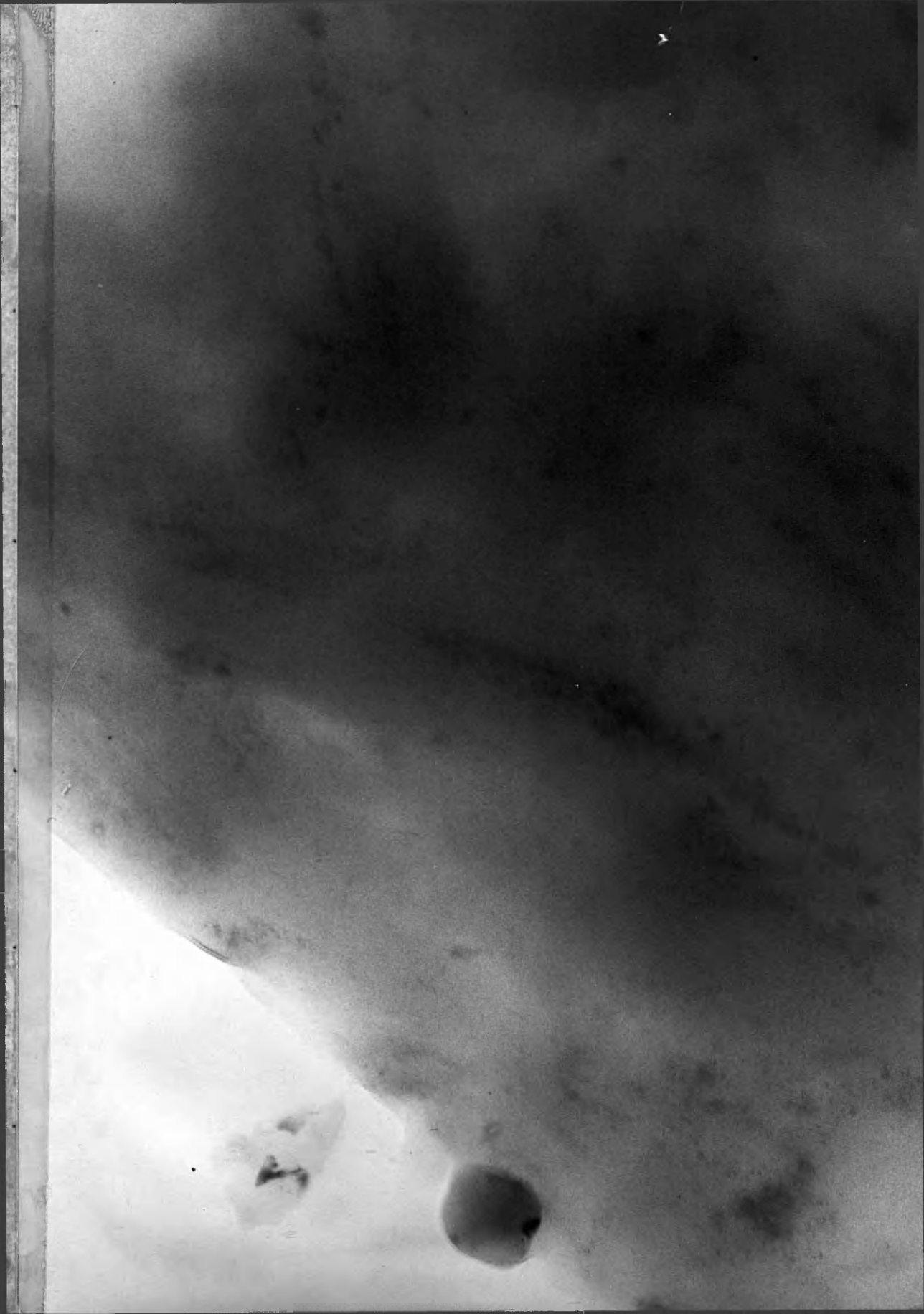


FIGURE 6.3

ELECTRON MICROGRAPH OF A SECTION OF A.M.F. A-104 MEMBRANE IN THE CHLORIDE FORM.

MAGNIFICATION X 170,000.



resolution down to values at which membrane structure should be apparent. There has been little electron microscopy done on ion exchange materials largely because of the technical difficulties involved. The fine structure of the membrane cannot be seen directly and special preparation of the sample is required. The exchanger is first loaded with simple or complex ions of heavy metals, the excess rinsed away and the sample dehydrated. (The technique demands that the sample be photographed in vacuo). It is then mounted in a plastic casting and sectioned. The position of the heavy atoms and hence the position of the functional groups in the exchanger are observed as dark regions in an otherwise unstained background of polymer. Figures 6.1 and 6.2 show two typical areas of a section of AMF A-104 membrane in the chromate form and Figure 6.3 shows another section in the chloride form. (The magnification of these samples is x 170,000 and so 1.7 millimetres represents 100 Ångstroms). At this scale the membranes studied show a remarkable degree of homogeneity. Other micrographs available in the literature (52)(54)(114)(115)(116)(117)(118)(119)(120)(121) show a distinct 'insular' structure not displayed here. The smooth gradations of shading, particularly on the chromate form micrographs, are caused by variations in the sample thickness. As the chromate ion is considerably heavier than chloride, contrast is much better on these micrographs. An obvious feature of the chromate micrographs, which is less marked in the chloride, is the presence of very dark spots varying in size from about 200 Ångstroms

down to the limits of detection. These spots are not artefacts of the experimental technique, as they appear only on the membrane and not on the support. They would seem to represent very localised areas of highly crosslinked material although just possibly they could be small inclusions of heavy metal left behind after the manufacturing process. The graininess visible on the micrographs on close examination is caused by enlargement of the photographic plates and is not evidence of heterogeneity in the membrane. All electron micrograph evidence here contradicts the electrolyte uptake evidence, which suggested that there was a fair degree of heterogeneity in the membrane ($Z=0.50$). It may be objected that the dehydration of the membrane to obtain electron micrographs invalidates comparisons between the two sets of evidence. The shrinkage on dehydration may have caused structural collapse and disappearance of voids. This is a real possibility but it should be noted that Goldring (119) uses exactly the opposite argument to explain the extreme heterogeneity evident in the micrographs of Grubhofer (115) and Crabtree and Glueckauf(52). As the membrane used here has a very low water content, dehydration may not have too drastic an effect on the structure and therefore, with reservations, the micrographs will be accepted as approximating to the membrane as it is during uptake experiments. The foregoing highlights a basic assumption made in the Glueckauf approach, i.e. that all deviations of $\tilde{\bar{m}}$ from that predicted by the Donnan expression are a consequence of heterogeneity. On the evidence here, this is not a good assumption.

6.3 Structural Analysis by the Glueckauf Method - Coion Permeability and Structure.

In section 6.1, equations permitting the calculation of the fractional distribution of sites within the exchanger were derived. The Glueckauf analysis does not end here and the treatment can be extended to predicting the permeability of coion in the exchanger. Several factors contributing to the diffusion of coion can be distinguished. The first, and perhaps most obvious, is the obstruction of coions by the polymer chains, which may be dealt with by applying the tortuosity correction discussed in section 4.2.1. The site distribution also plays a major role as the relative locations of regions of high and low M values determine to a large extent the magnitude of the coion flow. Thus a series of interconnecting regions of low M would be favourable for a large coion flow, and a few isolated low M regions in a high M background would be unfavourable. Given the magnitude of the coion flow and the fixed charge site distribution the Glueckauf analysis seeks to obtain information on the relative locations of areas of high and low fixed charge densities by obtaining a value of M, M^*, which corresponds to the molality of the most continuous region in the membrane. The treatment proceeds on the following lines.

The local permeability of any region of the exchanger is given by

$$P = \bar{D} \frac{\Delta \bar{c}}{\Delta c} \qquad (6.21)$$

Using a tracer technique to measure the permeability and maintaining the radioactive isotope concentration at zero on one side of the membrane, equation 6.21 becomes

$$P = \bar{D}\,\frac{\bar{c}}{c} \;\simeq\; \bar{D}\,\frac{\bar{m}}{m} \qquad (6.22)$$

$\bar{D}$ is the local diffusion coefficient within the exchanger, c and m refer to the aqueous solution concentrations of coion in molarities and molalities respectively, and $\bar{c}$ and $\bar{m}$ define the uptake of coion similarly. It should be noted that this defines the diffusion coefficient $\bar{D}$ slightly differently to that used previously. $\bar{c}$ is in moles per litre of membrane solution as against the more usual moles per litre of membrane, making Glueckauf's diffusion coefficient smaller by a factor v_w, the volume fraction of solution.

$\frac{\bar{m}}{m}$ can be readily substituted in terms of equation 6.3 and equation 6.2 can be rewritten as

$$P = \bar{D}.\left(-\frac{M}{m} + \sqrt{\frac{M^2}{m^2} + 4\alpha^2}\right) / 2 \qquad (6.23)$$

A mean value of the permeability for the whole membrane is obtained by integrating the Bruggeman equation (68)(123)

$$\frac{dP}{d(\ln u)} = \frac{3P(Pu-P)}{2P + Pu} \qquad (6.24)$$

where Pu is the permeability of the volume fraction between u and (u+du) which is being added to an already treated volume fraction u of overall permeability P. The procedure adopted is to choose a value of M^* with permeability P^* (from equation 6.23) and then to integrate

TABLE 6.4

GLUECKAUF PERMEABILITY CALCULATIONS

CASE 1 INTEGRATION SEQUENCE $M=M^* \rightarrow M=B$, $M=M^* \rightarrow M=0$

M^*	$P_{0.1}/P_{0.5}$	$P_{0.5}/P_{0.5}$	$P_{1.0}/P_{0.5}$	$P_{2.0}/P_{0.5}$
0.01	0.388	1.00	1.69	1.94
0.1	0.321	1.00	1.79	2.15
1.0	0.266	1.00	1.98	2.49
5.0	0.246	1.00	1.70	2.34
10.0	0.218	1.00	1.85	2.22
Experimental	0.447	1.00	1.37	1.78

CASE 2 INTEGRATION SEQUENCE $M=M^* \rightarrow M=0$, $M=M^* \rightarrow M=B$

M^*	$P_{0.1}/P_{0.5}$	$P_{0.5}/P_{0.5}$	$P_{1.0}/P_{0.5}$	$P_{2.0}/P_{0.5}$
0.01	0.457	1.00	1.72	2.04
0.1	0.458	1.00	1.73	2.06
1.0	0.431	1.00	1.75	2.09
5.0	0.284	1.00	1.57	1.95
10.0	0.247	1.00	2.03	2.20
Experimental	0.447	1.00	1.37	1.78

in the direction of M = B or M = A depending on which of the two is considered to correspond to the next most continuous region. The integration is completed by integrating from M^* to the other limit, taking the overall permeability from the first integration as the starting value of the second. The net result of this is to weight the final permeability in favour of the most continuous regions of the exchanger as the Bruggeman equation is not symmetrical. The computer program used for these calculations is reproduced in Appendix A.6.

Comparison of the generated permeabilities at different external solution concentrations derived from a given M^*, with the experimental values, is best done by dividing the former by one of their number and the latter by the corresponding experimental value. The advantage of comparing ratios is that tortuosity is eliminated from the calculations. The value of M^* which gives the best fit with experimental data is obtained by trial and error. Depending on its value deductions may be made about the geometrical arrangement of high or low M areas.

Results obtained when this treatment was applied to the experimental data were disappointing. No prejudgement was made as to the proper sequence of integration, both were tried, but a satisfactory fit with experimental values could not be obtained, as is shown in Table 6.4. Several reasons can be suggested. The most important is probably the large experimental error in $\tilde{m}$ which is carried over into α (equation o.16) and hence into the generated permeability. Secondly the permeability ratios are insensitive to changes in M^* at relatively

high concentrations and thirdly there are a limited number of data points. All these explanations are based on experimental factors, but the Glueckauf treatment itself, however, is open to several objections. By deliberate choice, all deviations from classical Donnan uptakes are ascribed solely to heterogeneity. In this work at least, the electron micrographs apparently cast some doubt on this assumption and as has been previously mentioned, work elsewhere in the literature (110)(111)(112)(113) predicts low coion activity coefficients as an intrinsic property of systems where double layers play an important role. Furthermore the Glueckauf theory has nothing whatever to say on systems with fixed charge - counterion interactions, which will greatly affect electrolyte uptake and coion diffusion. Heterogeneity must also make an important contribution in membranes, and may be the major contributor in a membrane of high water content, but in a tight membrane, and particularly in anion exchangers, the Glueckauf view is probably an oversimplification. Setting this problem aside, the major objection to the treatment, as it stands, is the distribution function itself which is derived on purely a priori grounds. There is clearly room for refinement here.

CHAPTER 7

CHLORIDE/IODIDE SELECTIVITY MEASUREMENTS

Up to now attention has been concentrated on the measurement and interpretation of transport properties, but a study of equilibrium properties can provide useful information and illuminate certain aspects of behaviour which are less amenable to study through transport processes. Foremost among these is the matrix-counterion interaction which has been the subject of much discussion in previous chapters. Fixed ion-counterion interactions affect the values of the phenomenological coefficients and many useful deductions can be made. Nevertheless it is not a good method of studying these phenomena in ion exchangers. The relative affinity of the exchanger for the iodide ion against chloride can however be measured accurately and a number of selectivity measurements were made on the membrane in equilibrium with a series of solutions containing sodium chloride and sodium iodide at an overall ionic strength of 0.1 molar. Previous work (124)(125)(126)(127)(128)(129) has shown that at low and medium ionic strengths anion exchangers invariably prefer iodide to chloride (as might be expected on the basis of the discussion of section 1.3) but there is less agreement on the degree of the preference. Particularly interesting in this respect is that some of the previous measurements have been made on Dowex-2 anion exchange beads (126)(127) which have the same quaternary ammonium fixed group as AMF A-104 membranes. Before discussing the results, however, it is necessary to define more precisely the information which can be obtained from a study of selectivity.

7.1 The Selectivity Coefficient and Rational Equilibrium Constant

The selectivity coefficient K^I_{Cl} is usually defined as

$$K^I_{Cl} = \frac{\bar{X}_I}{\bar{X}_{Cl}} \cdot \frac{X_{Cl}}{X_I} \qquad (7.1)$$

where $\bar{X}_I$ and $\bar{X}_{Cl}$ represent the mole fractions of these ions in the membrane phase and the unbarred symbols represent the same quantities in the solution phase. A corrected selectivity coefficient is often defined which includes the solution activity coefficients, but in this case where the overall ionic strength was maintained at 0.1 molar, the activity coefficient ratio is virtually unity. K^I_{Cl} is not a true equilibrium constant but rather a relative affinity coefficient and may vary with the relative proportion of the ions. If membrane phase activity coefficients $\bar{f}_{Cl}$ and $\bar{f}_I$ are defined in an analogous manner to the solution activity coefficients, i.e. if the same standard states are used for the membrane and the solution, then

$$\frac{\bar{X}_I}{\bar{X}_{Cl}} \cdot \frac{X_{Cl}}{X_I} \cdot \frac{\bar{f}_I}{\bar{f}_{Cl}} = 1 = K^I_{Cl} \cdot \frac{\bar{f}_I}{\bar{f}_{Cl}} \qquad (7.2)$$

and thus K^I_{Cl} is simply the ratio of the membrane phase activity coefficients (94).

Another approach which has been adopted is to define the standard and reference states of the exchanger phase to be the respective monoionic forms in equilibrium with pure water. With this convention, the rational equilibrium constant $\tilde{K}^I_{Cl}$ may be written

$$\tilde{K}^I_{Cl} = \frac{\bar{X}_I}{\bar{X}_{Cl}} \cdot \frac{X_{Cl}}{X_I} \cdot \frac{\bar{f}_I}{\bar{f}_{Cl}} = K^I_{Cl} \cdot \frac{\bar{f}_I}{\bar{f}_{Cl}} \qquad (7.3)$$

$\tilde{K}^I_{Cl}$ is defined as a constant and therefore $\frac{\bar{f}_I}{\bar{f}_{Cl}}$ contains the variation of K^I_{Cl} with composition. A completely general thermodynamic treatment using rational activities in the membrane phase has been given by Gaines and Thomas (130). Making use of the observations that coion uptake is negligible and the water activity in the solution remains essentially constant over the range $0 \leq X_I \leq 1$ at an overall ionic strength of 0.1 molar, the general equation given by these authors can be reduced to

$$\ln \tilde{K}^I_{Cl} = (N^w_I - N^w_{Cl}) \ln a_w + \int_0^1 \ln K^I_{Cl} \, d\bar{X}_I \qquad (7.4)$$

where N^w_{Cl} and N^w_I are the number of moles of water per equivalent of fixed ionic groups in the pure chloride and iodide forms respectively. In the notation used in earlier chapters the N^w's are given by c_3/c_4 in the pure forms.

A fuller description of quantitative theories of selectivity is given by Helfferich (131), Reichenberg (132) and Holm (133).

7.2 Results and Discussion

The mole fractions of the chloride and the iodide in the membrane were determined by the radiochemical technique described in section 3.7 and Appendix A.5. The membrane was first equilibrated in 0.1 molar sodium chloride and the total halide content of the membrane obtained by the uptake of Cl^{36} tracers. In succeeding experiments, as X_I was increased from zero towards unity, the chloride content was measured directly, as before, and the iodide content obtained by difference. Great care had to be taken when the membrane was equilibrated with a solution containing a new X_I/X_{Cl} ratio, especially at low X_I. Normal procedure was to allow

TABLE 7.1

SELECTIVITY COEFFICIENTS

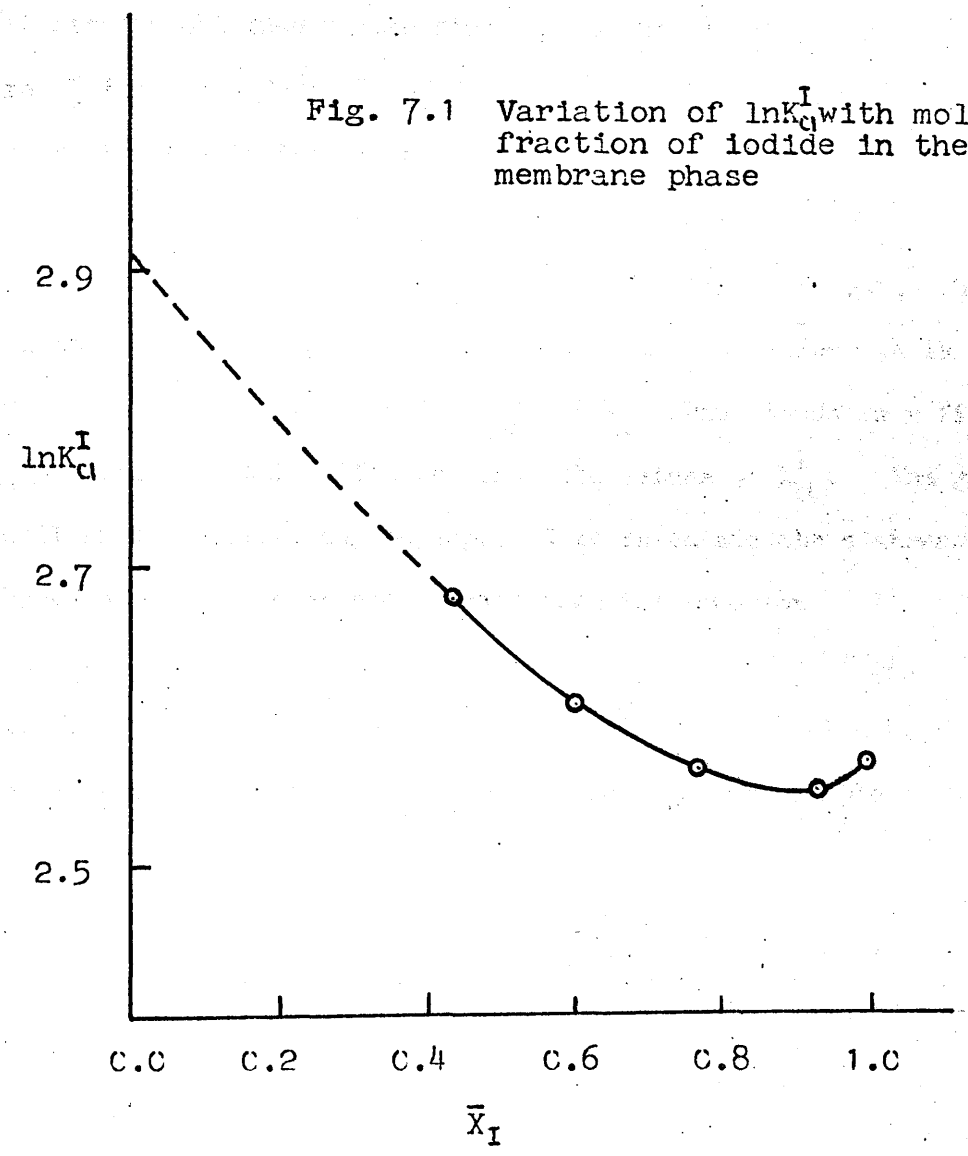
X_{Cl}	X_I	$\bar{X}_{Cl}$	$\bar{X}_I$	K^I_{Cl}	$\ln K^I_{Cl}$
0.950	0.050	0.566	0.434	14.54	2.677
0.900	0.100	0.399	0.601	13.58	2.609
0.800	0.200	0.235	0.765	13.00	2.565
0.500	0.500	0.072	0.928	12.80	2.549
0.100	0.900	0.008	0.992	13.06	2.570

TABLE 7.2

OSMOTIC DESWELLING

X_{Cl}/X_I	meq.Cl	meq.I	meq.H_2O	Δ meq.H_2O/Δ meq.I
1.00/0.00	0.286	0.000	2.49	
				- 4.3
0.95/0.05	0.162	0.124	1.96	
				- 4.0
0.90/0.10	0.114	0.172	1.77	
				- 4.3
0.80/0.20	0.067	0.219	1.57	
				- 4.5
0.50/0.50	0.021	0.265	1.36	
				- 6.6
0.10/0.90	0.002	0.284	1.24	
				-16.6
0.00/1.00	0.000	0.286	1.20	

Fig. 7.1 Variation of $\ln K_{Cl}^{I}$ with mole fraction of iodide in the membrane phase



membrane equilibration in two or three 50 ml aliquots of the new solution, but the preference of the exchanger for iodide ions was such that at low iodide loadings, it could remove a substantial fraction of the iodide from 50 ml of solution and drastically alter X_I/X_{Cl}. In solutions where this effect was significant it was found necessary to allow equilibration with four to six 50 ml aliquots. To avoid the problem completely the pure iodide form should be converted progressively to the pure chloride form, but this is less experimentally convenient when using Cl^{36} tracers. The results obtained in the study are shown in Table 7.1 and the $\ln K^I_{Cl}$ are plotted as a function of $\bar{X}_I$ in Figure 7.1. To permit calculation of the rational equilibrium constant of equation 7.4 the values of $\ln K^I_{Cl}$ were fitted to a polynomial of the type $y = a + b\bar{X}_I + c\bar{X}_I^2$ by a least squares curve fitting procedure and the function integrated between the limits 0 and 1. The term for the solvent in equation 7.4 is positive, but small in comparison to $\int \ln K^I_{Cl} \; d\bar{X}_I$, which leads to a final value of $\tilde{K}^I_{Cl}$ of 14.1 - little different from the values of K^I_{Cl}. The rational equilibrium constant may be employed to calculate the standard free energy change of the ion exchange process from the equation

$$\triangle G^o = - RT \ln \tilde{K}^I_{Cl} \qquad (7.5)$$

With the value of $\tilde{K}^I_{Cl}$ above, $\triangle G^o$ = -6,560 joules or -1.6 K.cal. which means that the iodide form of the membrane is more stable than the chloride form by 1.6 K.cal.

As mentioned above, selectivity measurements have been carried out on Dowex-2 anion exchange beads (126)(127) which have the same exchange groups as AMF A-104 membranes. Gregor, Belle and Marcus (127) find values of K^I_{Cl} ranging from 9.6 to 16 as the d.v.b. content of the resin

rises from 1 to 16 per cent while Wheaton and Bauman (126) obtain a value of 7 in a resin with an 8 per cent d.v.b. content, which is roughly 50 per cent of the corresponding value of Gregor and coworkers. As shown in Table 7.1, values of K^{I}_{Cl} fall between 12.8 and 14.5. The graph of $\ln K^{I}_{Cl}$ against $\bar{X}_I$ is unusual in that it shows a minimum. For a system such as that studied, where ion association appears to be important for one counterion (iodide) and not the other, the expected graph (in the absence of pressure-volume effects) would show a steady decrease in K^{I}_{Cl} as the mole fraction of iodide in the exchanger increased (127). The observation that the preference of the exchanger for iodide increases again at high values of $\bar{X}_I$ suggests that an extra factor must be involved - possibly the pressure-volume effects ignored by Gregor and coworkers. At high mole fractions of iodide the membrane phase becomes very condensed ($\sim$14M) and will therefore experience a considerable swelling pressure. It would be expected under these circumstances that the exchanger would show an increased preference for the ion which could be incorporated into the system with the least work.

The osmotic deswelling of the membrane was investigated further by measuring the wet weight, as described in section 3.3.1, at each equilibrium concentration. With this information it is possible to calculate the average number of molecules of water which leave the membrane when a chloride ion is replaced by an iodide ion. The results are displayed in Table 7.2. Over a considerable fraction of the range, up to $X_I = 0.5$, the ratio $\triangle$ meq. water/$\triangle$ meq. iodide varies little, but at higher iodide loadings there is a rapid increase.

As the chemical potential of the water remains essentially constant throughout, variations in this term are not the cause. It is noticeable, however, that the increase in the Δ meq. water/ Δ meq. iodide ratio coincides almost exactly with the rise in K_{Cl}^{I} and the two may be interdependent.

BIBLIOGRAPHY

1. B.J. ZWOLINSKI, H.EYRING AND C.E. REESE, J. Phys. Chem., 53 1426 (1949).

2. I. PRIGOGINE, "Introduction to the Thermodynamics of Irreversible Processes", Thomas, Springfield, Illinois, 1955.

3. D.D. FITTS, "Nonequilibrium Thermodynamics", McGraw-Hill, New York, 1962.

4. S.R. DE GROOT AND P. MAZUR, "Non Equilibrium Thermodynamics", North Holland, Amsterdam; Wiley, New York, 1962.

5. A. KATCHALSKY AND P. CURRAN, " Nonequilibrium Thermodynamics in Biophysics", Harvard University Press, Cambridge, Mass., U.S.A., 1965.

6. F. HELFFERICH, "Ion Exchange", McGraw-Hill, New York, 1962.

7. Reference (5), Chapter 4.

8. Reference (5), Chapter 7.

9. L. ONSAGER, Phys. Rev., 37 405 (1931).

10. L. ONSAGER, Phys. Rev., 38 2265 (1931).

11. J.G. KIRKWOOD, "Ion Transport Across Membranes", Academic Press, New York, 1954, P. 119.

12. D.G. MILLER, Chem. Rev. 60 15 (1960).

13. A.J. STAVERMAN, Trans. Faraday Soc., 48 176 (1952).

14. P.B. LORENZ, J. Phys. Chem., 56 775 (1952).

15. K.S. SPIEGLER, Trans. Faraday Soc., 54 1408 (1958).

16. G.J. HILLS, P.W.M. JACOBS AND N. LAKSHMINARAYANAIAH, Proc. Roy. Soc. (London), A262 246 (1961).

17. O. KEDEM AND A. KATCHALSKY, J. Gen. Physiol. 45 143 (1961).

18. O. KEDEM AND A. KATCHALSKY, Trans. Faraday Soc., 59 1918 (1963).

19. D.G. MILLER, J. Phys. Chem., 70 2639 (1966).

20. Reference (6), P. 326

21. S.LJUNGGREN, Trans. Roy. Inst. Technol. Stockholm, 172 1 (1961).

22. Reference (5), p. 129

23. P.J. DUNLOP, J. Phys. Chem., 68 26 (1964).

24. R.W. LAITY, J. Phys. Chem., 67 671 (1963).

25. O. KEDEM, "Membrane Transport and Metabolism", eds. A. Kleinzellar and A. Kotyk, Academic Press, New York, 1960.

26. P. MEARES, Trans. Faraday Soc., 55 970 (1959).

27. R. PATERSON, "Membranes and Ion Transport", ed. E.E. Bittar, Wiley New York, 1970.

28. E.M. SCATTERGOOD AND E.N. LIGHTFOOT, Trans. Faraday Soc., 64 1135 (1968).

29. O. KEDEM AND A. ESSIG, J. Gen. Physiol. 48 1047 (1965).

30. Reference (6), p.344.

31. Reference (6), p. 268.

32. Reference (6), p. 230.

33. G.A. BRAY, Anal. Biochem., 1 279 (1960).

34. D. MACKAY AND P. MEARES, Trans. Faraday Soc., 55 1221 (1959).

35. P. MEARES, J. Appl. Polymer Sci. 9 917 (1965).

36. Reference (6), p. 315.

37. E. GLUECKAUF AND R.E. WATTS, Proc. Roy. Soc. (London), A268 339 (1962).

38. R. ARNOLD AND D.F.A. KOCH, Aust. J. Chem. 19 1299 (1966).

39. G.J. HILLS, A.O. JAKUBOVIC AND J.A. KITCHENER, J. Polymer Sci., 19 382 (1956).

40. P. MEARES AND H.H. USSING, Trans. Faraday Soc. 55 244 (1959).

41. V. SUBRAHMANYAN AND N. LAKSHMINARAYANAIAH, J. Phys. Chem., 72 4314 (1968).

42. J.H. GEORGE AND R.A. COURANT, J. Phys. Chem., 71 246 (1967).

43. D.K. HALE AND D.J. MCCAULEY, Trans. Faraday Soc., 57 135 (1961).

44. H.P. GREGOR, R.A. KRAMER, A. LALIK, V. HOLSTROM AND T. SABER, Membrane Evaluation Program, New York, Brooklyn Polytechnic, 1961.

45. "Test Manual for Permselective Membranes", U.S. Office of Saline Water Research, Report No. 77, January 1964, P.B. 181575.

46. R.M. BARRER, J.A. BARRIE AND M.G. ROGERS, Trans. Faraday Soc., 58 2473 (1962).

47. N. LAKSHMINARAYANAIAH, Chem. Rev. 65 492 (1965).

48. D.G.J. IVES AND G.J. JANZ, "Reference Electrodes, Theory and Practice", Academic Press, 1961 p. 205.

49. G. GRAN, Analyst 77 661 (1952).

50. Reference (6), Chapter 4.

51. E.L. CHRISTENSEN, Ph.D. Thesis, University of Wisconsin, 1968.

52. J.M. CRABTREE AND E. . GLUECKAUF, Trans. Faraday Soc. 59 2639 (1963).

53. E.M. SCATTERGOOD, Ph.D. Thesis, University of Wisconsin, 1966.

54. C.R. GARDNER, Ph.D. Thesis, University of Glasgow, 1970.

55. A. WHEELER, Advances in Catalysis 3 249 (1951).

56. J.S. MACKIE AND P. MEARES, Proc. Roy. Soc. (London) A232 498 (1955).

57. S. PRAGER, J. Chem. Phys. 33 122 (1960).

58. P. MEARES, "Diffusion in Polymers", eds. J. Crank and G.S. Park, Academic Press, London, 1968.

59. A. DESPIC AND G.J. HILLS, Trans. Faraday Soc., 53 1262 (1957).

60. A.O. JAKUBOVIC, G.J. HILLS AND J.A. KITCHENER, J. Chim. Phys., 55 263 (1958).

61. A.E. LAGOS AND J.A. KITCHENER, Trans. Faraday Soc. 56 1245 (1960).

62. J.H. WANG, C.V. ROBINSON AND I.S. EDELMAN, J. Amer. Chem. Soc., 75 466 (1953).

63. R. SCHLÖGL, Z. Elektrochem. 57 195 (1953).

64. M.A. PETERSON AND H.P. GREGOR, J. Electrochem. Soc., 106 1051 (1959).

65. W.J. MCHARDY, P. MEARES AND J.F. THAIN, J. Electrochem. Soc., 116 920 (1969).

66. J.H. WANG AND S. MILLER, J. Amer. Chem. Soc., 74 1611 (1952).

67. J.H. WANG, J. Amer. Chem. Soc., 74 1612 (1952).

68. E. GLUECKAUF, Proc. Roy. Soc. (London) A268 350 (1962).

69. R.L. GUSTAFSON, J. Phys. Chem., 67 2549 (1963).

70. R.L. GUSTAFSON, J. Phys. Chem., 70 957 (1966).

71. K.S. SPIEGLER, Unpublished, 1954, quoted in reference (6).

72. "Handbook of Electrochemical Constants" compiled by R. Parsons, Butterworths, London, 1959.

73. Reference (6), p. 115.

74. J. MOLENAT, J. Chim. Phys. 66 825 (1966).

75. A.G. WINGER, R. FERGUSON AND R. KUNIN, J. Phys. Chem., 60 556 (1956).

76. R.J. STEWART AND W.F. GRAYDON, J. Phys. Chem., 61 164 (1957).

77. P. MEARES AND A.H. SUTTON, J. Coll. Interface Sci. 28 118 (1968).

78. H. KRÄMER AND P. MEARES, Biophys. J., 9 1006 (1969).

79. C.R. GARDNER AND R. PATERSON, J. Chem. Soc., in press.

80. D.G. MILLER, J. Phys. Chem., 71 616 (1967).

81. W. DORST, A.J. STAVERMAN AND R. CARAMAZZA, Rec. Trav. Chim., 83 1329 (1964).

82. R.W. GURNEY, "Ionic Processes in Solution", McGraw-Hill, New York, 1953.

83. S. LAPANJE AND S.A. RICE, J. Amer. Chem. Soc., 83 496 (1961).

84. L. KOTIN AND M. NAGASAWA, J. Amer. Chem. Soc., 83 1026 (1961).

85. J.E. GORDON, Chem. and Ind. (London), 1962,267.

86. R.H. DINIUS, M.T. EMERSON AND G.R. CHOPPIN, J. Phys. Chem., 67 1178 (1963).

87. R.H. DINIUS AND G.R. CHOPPIN, J. Phys. Chem., 68 425 (1964).

88. D. REICHENBERG AND I.J. LAWRENSON, Trans. Faraday Soc., 59 141 (1963).

89. U.P. STRAUSS AND Y.P. LEUNG, J. Amer. Chem. Soc., 87 1476 (1965).

90. O. KEDEM AND S.R. CAPLAN, Trans. Faraday Soc., 61 1897 (1965).

91. S.R. CAPLAN, J. Theoret.Biol., 10 209 (1966).

92. S.R. CAPLAN, J. Phys. Chem., 69 3801 (1965).

93. J. GUTKNECHT, Science 158 787 (1967).

94. W.C. BAUMAN AND J. EICHHORN, J. Amer. Chem. Soc., 69 2830 (1947).

95. H.P. GREGOR, F. GUTOFF AND J.I. BREGMAN, J. Coll. Sci., 6 245 (1951).

96. H.P. GREGOR AND M.H. GOTTLIEB, J. Amer. Chem. Soc., 75 3539 (1953).

97. C.W. DAVIES AND G.D. YEOMAN, Trans. Faraday Soc., 49 968 (1953).

98. J.S. MACKIE AND P. MEARES, Proc. Roy. Soc. (London), A232 485 (1955).

99. G.J. HILLS, P.W.M. JACOBS AND N. LAKSHMINARAYANAIAH, Proc. Roy. Soc. (London), A262 257 (1961).

100. K.A. KRAUS AND G.E. MOORE, J. Amer. Chem. Soc., 75 1457 (1953).

101. M.H. GOTTLIEB AND H.P. GREGOR, J. Amer. Chem. Soc., 76 4639 (1954).

102. F. NELSON AND K.A. KRAUS, J. Amer. Chem. Soc., 80 4154 (1958).

103. J. DANON, J. Phys. Chem., 65 2039 (1961).

104. D.H. FREEMAN, J. Phys. Chem., 64 1048 (1960).

105. A. KATCHALSKY AND S. LIFSON, J. Polymer Sci., 11 409 (1953).

106. U.P. STRAUSS AND P. ANDER, J. Amer. Chem. Soc., 80 6494 (1958).

107. Z. ALEXANDEROWICZ, J. Polymer Sci. 56 115 (1962).

108. M. NAGASAWA, M. IZUMI AND I. KAGAWA, J. Polymer Sci., 37 375 (1959).

109. J.A. MARINSKY, "Ion Exchange Volume 1", J.A. Marinsky (ed.), Edward Arnold, London, 1966, Chapter 9.

110. L. LAZARE, B.R. SUNDHEIM AND H.P. GREGOR, J. Phys. Chem., 60 641 (1956).

111. M.G.T. SHONE, Trans. Faraday Soc., 58 805 (1962).

112. L. DRESNER AND K.A. KRAUS, J. Phys. Chem., 67 990 (1963).

113. L. DRESNER, J. Phys. Chem., 67 2333 (1963).

114. E. BLASIUS, H. PITTACK AND M. NEGWER, Angew. Chem., 68 671 (1956).

115. N. GRUBHOFER, Makromol. Chem., 30 96 (1959).

116. L.S. GOLDRING, Abstr. 142nd. meeting Amer. Chem. Soc., Atlantic City, N.J., 1962.

117. K. LITTLE, Proc. Roy. Soc. (London), A268 370 (1962).

118. F. DE KOROSY, Nature 198 882 (1963).

119. L.S. GOLDRING, "Ion Exchange Volume 1", J.A. Marinsky (ed.), Edward Arnold, London, 1966, Chapter 6.

120. M. BLOCK, Chem. Ind. 50 2099 (1967).

121. J. KLINOWSKI AND M. LESZKO, Roczniki. Chem., 42 123 (1968).

122. R. ARNOLD, Aust. J. Chem., 21 521 (1968).

123. D.A.G. BRUGGEMAN, Ann. Phys. Lpz., 24 636 (1935).

124. R. KUNIN AND F.X. MCCARTHY, Ind. Eng. Chem., 41 12 (1949).

125. R.W. ATTERBURY AND G.E. BOYD, J. Amer. Chem. Soc., 72 4805 (1950).

126. R.M. WHEATON AND W.C. BAUMAN, Ind. Eng. Chem., 43 1088 (1951).

127. H.P. GREGOR, J. BELLE AND R.A. MARCUS, J. Amer. Chem. Soc., 77 2713 (1955).

128. G.E. BOYD, S. LINDENBAUM AND G.E. MYERS, J. Phys. Chem., 65 577 (1961).

129. R.M. DIAMOND AND D.C. WHITNEY, "Ion Exchange Volume 1", J.A. Marinsky (ed.) Edward Arnold, London, 1966 Chapter 8.

130. G.L. GAINES JR. AND H.C. THOMAS, J. Chem. Phys. 21 714 (1953).

131. Reference (6), Chapter 5.

132. D. REICHENBERG, "Ion Exchange Volume 1", J.A. Marinsky (ed.), Edward Arnold, London, 1966, Chapter 7.

133. L.W. HOLM, Arkiv. Kemi., 10 151, 445, 461 (1957).

APPENDIX A.1

SOLVENT FIXED MOBILITY COEFFICIENTS

Starting from equations 2.11

$$T\sigma = \sum_{i=1}^{4} J_i X_i \qquad (2.11)$$

and 2.13

$$\sum_{i=1}^{4} c_i X_i = 0 \qquad (2.13)$$

the latter equation can either be used to eliminate X_4 from equation 2.11 and so give the phenomenological equations appropriate to the membrane fixed frame of reference.

$$(J_1 - \frac{c_1}{c_4} J_4) = \ell_{11}X_1 + \ell_{12}X_2 + \ell_{13}X_3 \qquad (A.1.1a)$$

$$(J_2 - \frac{c_2}{c_4} J_4) = \ell_{21}X_1 + \ell_{22}X_2 + \ell_{23}X_3 \qquad (A.1.1b)$$

$$(J_3 - \frac{c_3}{c_4} J_4) = \ell_{31}X_1 + \ell_{32}X_2 + \ell_{33}X_3 \qquad (A.1.1c)$$

or alternatively eliminate X_3 and give the solvent fixed phenomenological equations

$$(J_1 - \frac{c_1}{c_3} J_3) = L_{11}X_1 + L_{12}X_2 + L_{14}X_4 \qquad (A.1.2a)$$

$$(J_2 - \frac{c_2}{c_3} J_3) = L_{21}X_1 + L_{22}X_2 + L_{24}X_4 \qquad (A.1.2b)$$

$$(J_4 - \frac{c_4}{c_3} J_3) = L_{41}X_1 + L_{42}X_2 + L_{44}X_4 \qquad (A.1.2c)$$

If X_3 is eliminated from equations A.1.1a-c, using equation 2.13, and the terms collected, they may be rewritten

$$(J_1 - \frac{c_1}{c_4} J_4) = (\ell_{11} - \frac{c_1}{c_3} \ell_{13}) X_1 + (\ell_{12} - \frac{c_2}{c_3} \ell_{13}) X_2 - \frac{c_4}{c_3} \ell_{13} X_4 \qquad \text{(A.1.3a)}$$

$$(J_2 - \frac{c_2}{c_4} J_4) = (\ell_{21} - \frac{c_1}{c_3} \ell_{23}) X_1 + (\ell_{22} - \frac{c_2}{c_3} \ell_{23}) X_2 - \frac{c_4}{c_3} \ell_{23} X_4 \qquad \text{(A.1.3b)}$$

$$(J_3 - \frac{c_3}{c_4} J_4) = (\ell_{31} - \frac{c_1}{c_3} \ell_{33}) X_1 + (\ell_{32} - \frac{c_2}{c_3} \ell_{33}) X_2 - \ell_{33} \frac{c_4}{c_3} X_4 \qquad \text{(A.1.3c)}$$

These equations may be made formally identical to equations A.1.2a-c by subtracting $\frac{c_1}{c_3}$ x equation A.1.3c from equation A.1.3a, subtracting $\frac{c_2}{c_3}$ x equation A.1.3c from equation A.1.3b and finally multiplying equation A.1.3c all through by $-\frac{c_4}{c_3}$.

By equating coefficients in these resultant equations with those of equations A.1.2a-c the following expressions for L coefficients in terms of ℓ coefficients are obtained.

$$L_{11} = \ell_{11} - 2. \frac{c_1}{c_3} \ell_{13} + \frac{c_1^2}{c_3^2} \ell_{33} \qquad \text{(A.1.4)}$$

$$L_{12} = \ell_{12} - \frac{c_2}{c_3} \ell_{13} - \frac{c_1}{c_3} \ell_{23} + \frac{c_1 c_2}{c_3^2} \ell_{33} \qquad \text{(A.1.5)}$$

$$L_{22} = \ell_{22} - 2 \frac{c_2}{c_3} \ell_{23} + \frac{c_2^2}{c_3^2} \ell_{33} \qquad \text{(A.1.6)}$$

$$L_{14} = \frac{c_1 c_4}{c_3^2} \ell_{33} - \frac{c_4}{c_3} \ell_{13} \qquad \text{(A.1.7)}$$

$$L_{24} = \frac{c_2 c_4}{c_3^2} \ell_{33} - \frac{c_4}{c_3} \ell_{23} \qquad \text{(A.1.8)}$$

$$L_{44} = \frac{c_4^2}{c_3^2} \ell_{33} \qquad \text{(A.1.9)}$$

Similarly

$$\ell_{11} = L_{11} - 2.\frac{c_1}{c_4} L_{14} + \frac{c_1^2}{c_4^2} L_{44} \qquad \text{(A.1.10)}$$

$$\ell_{12} = L_{12} - \frac{c_2}{c_4} L_{14} - \frac{c_1}{c_4} L_{24} + \frac{c_1 c_2}{c_4^2} L_{44} \qquad \text{(A.1.11)}$$

$$\ell_{22} = L_{22} - 2 \frac{c_2}{c_4} L_{24} + \frac{c_2^2}{c_4^2} L_{44} \qquad \text{(A.1.12)}$$

$$\ell_{13} = \frac{c_1 c_3}{c_4^2} L_{44} - \frac{c_3}{c_4} L_{14} \qquad \text{(A.1.13)}$$

$$\ell_{23} = \frac{c_2 c_3}{c_4^2} L_{44} - \frac{c_3}{c_4} L_{24} \qquad \text{(A.1.14)}$$

$$\ell_{33} = \frac{c_3^2}{c_4^2} L_{44} \qquad \text{(A.1.15)}$$

APPENDIX A.2

E.M.F. OF A CONCENTRATION CELL AND CALCULATION OF X_1 AND X_2

a). E.M.F. of a Concentration Cell

In a cell such as that represented by figure A.2.1, where an ion exchange membrane separates two aqueous solutions of the same 1:1 electrolyte on sides ' and " respectively, salt and water flows occur in opposite directions and a diffusion potential is set up. If the assumption is made that there is no interfacial resistance at the membrane surface then the total potential, E, measured between the electrodes is given by

$$E = E_1 + E_m + E_2 \qquad (A.2.1)$$

The membrane will be chosen to be an anion exchanger and the electrodes reversible to the counterion so that

$$E_1 = - RT/F \ln a_1' \qquad (A.2.2a)$$

$$E_2 = - RT/F \ln (1/a_1'') \qquad (A.2.2b)$$

The diffusion potential, E_m, is given by the integral of equation 2.31 across the entire membrane, viz.

$$E_m = RT/F \left(t_1/z_1 \ln (a_1''/a_1') + t_2/z_2 \ln (a_2''/a_2') + t_3 \ln (a_3''/a_3')\right) \qquad (A.2.3)$$

Strictly speaking, t_1, t_2 and t_3 in equation A.2.3 are the mean values of the transport and water transference numbers of the membrane over the concentration interval $a'_i \rightarrow a_i''$ $(i=1,2,3)$ but providing the concentration gradients are small, the variation in the t_i across the membrane should be negligible.

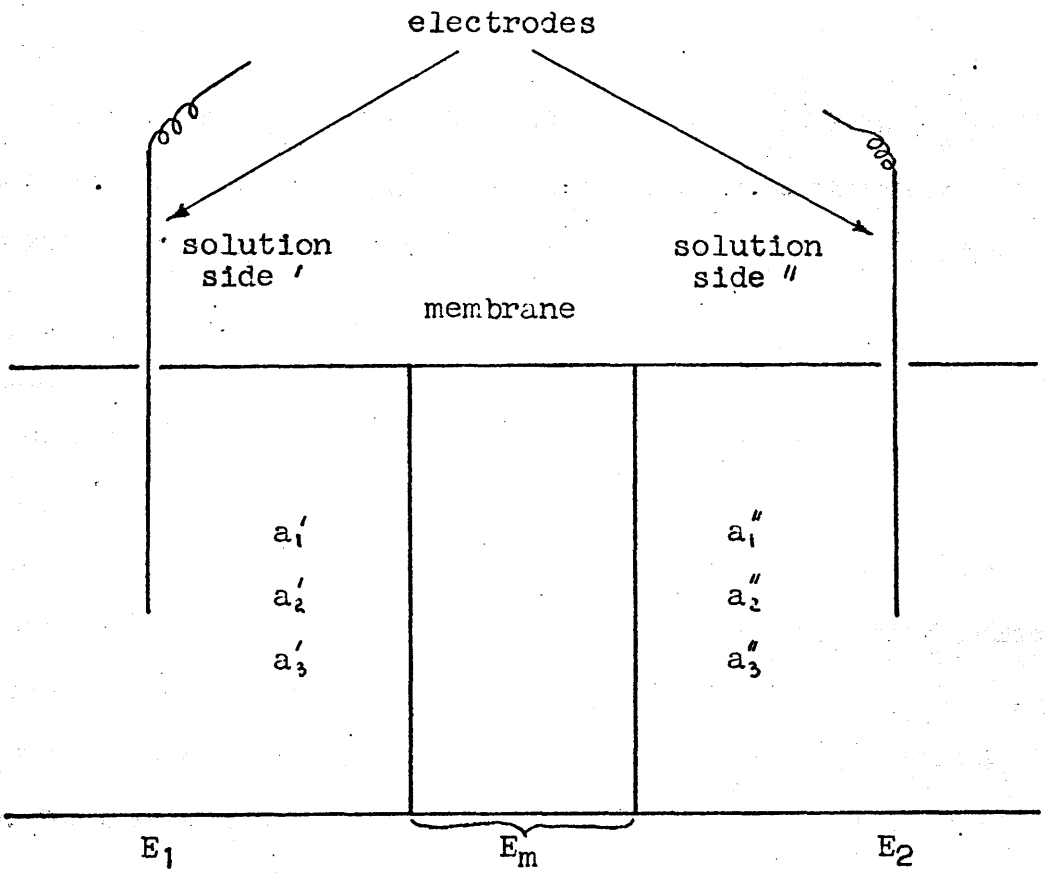


Fig. A.2.1 Schematic representation of membrane concentration cell

Substituting $t_1 = 1-t_2$, $z_1 = -1$, $z_2 = +1$ and rearranging, equation A.2.3 becomes

$$E_m = RT/F\ (t_2 \ln (a_1''.a_2''/a_1'.a_2'') + t_3 \ln (a_3''/a_3') - \ln (a_1''/a_1')) \quad (A.2.4)$$

and since $a_1''.a_2'' = (a''_{\pm})^2$ and $a_1'.a'_2 = (a'_{\pm})^2$ the equation may be rewritten

$$E_m = 2RT/F.t_2.\ln (a_{\pm}''/a_{\pm}') + RT/F.t_3.\ln (a_3''/a_3') - RT/F \ln (a_1''/a_1') \quad (A.2.5)$$

The total cell potential E given by equation A.2.1 is therefore

$$E = 2RT/F.t_2.\ln (a_{\pm}''/a_{\pm}') + RT/F.t_3.\ln (a_3''/a_3') \quad (A.2.6)$$

b) Calculation of X_1 and X_2

The electrochemical potential of the salt, $\tilde{u}_{12}$, is defined as

$$\tilde{u}_{12} = \tilde{u}_1 + \tilde{u}_2 \quad (A.2.7)$$

where $\tilde{u}_1$, $\tilde{u}_2$ are the electrochemical potentials of anion and cation respectively. If $\tilde{u}_1$ and $\tilde{u}_2$ are separated into chemical and electrical components and terms collected, then

$$\tilde{u}_{12} = u_1 + u_2 + (z_1 + z_2)\ F.\phi \quad = u_1 + u_2 = u_{12} \quad (A.2.8)$$

i.e. for a symmetrical electrolyte the chemical and electrochemical potentials of the salt are identical. This identity can be used to calculate X_1 and X_2 since

$$\left(-\frac{\partial \tilde{u}_{12}}{\partial x}\right) = \left(-\frac{\partial \tilde{u}_1}{\partial x}\right) + \left(-\frac{\partial \tilde{u}_2}{\partial x}\right) = X_1 + X_2 = \left(-\frac{\partial u_{12}}{\partial x}\right) \quad (A.2.9)$$

Equation A.2.9 in conjunction with equation 2.30, which may be written,

$$t_1/z_1.X_1 + t_2/z_2.X_2 + t_3.\ln (a_3''/a_3') = 0 \quad (2.30)$$

leaves X_1 and X_2 as the only unknowns, and the equations may therefore be solved for these quantities.

APPENDIX A.3

EFFECT OF SAMPLING ON MEASURED TRACER FLOWS

Consider a half cell of volume vo into which tracer ions are diffusing at an instantaneous rate of inc, where inc is some function of time. If the half cell is sampled to determine the activities at given times, then volume changes and/or dilution effects will result, giving an incorrect plot of activity against time. Ideally it is desired to sample without disturbing the system, so that a correct plot is obtained. The undisturbed system will therefore be taken as a reference. In the general derivation below the deviation from this ideality due to any form of sampling is calculated.

Let the volume of the sample removed be nn and let a be the volume of inactive solution added. (This means that the sample removed can be as large as necessary without ultimately causing a potentially catastrophic reduction in the volume of the sampling side).

Consider first the $i-1^{th}$ sample.

Activity / sample = $y[i-1]$

Volume when $i-1^{th}$ sample taken = $vo - (i-2) \times (nn-a)$

Time at which sample taken = $x[i-1]$

Volume after sample removed = $vo - (i-1) \times (nn-a) - a$

Total activity remaining = $y[i-1] \times (vo - (i-1) \times (nn-a) - a)/nn$

Volume a of inactive solution is added, therefore the volume of the system now becomes $vo - (i-1) \times (nn-a)$

The i^{th} sample is taken at time $x[i]$

Between $x[i-1]$ and $x[i]$, tracer has been diffusing into the half cell and the total activity added during this time interval is

$$vo/nn \times \int_{x\,[i-1]}^{x\,[i]} inc\,[i]\,dx$$

Note that the units of inc [i] are activity/unit time/ml (referred to the standard volume vo)/ sample.

Therefore at time x [i] the activity/sample is

$$\frac{y\,[i-1] \times (vo - (i-1) \times (nn-a) - a) + vo \times \int_{x\,[i-1]}^{x\,[i]} inc\,[i]\,dx}{vo - (i-1) \times (nn-a)} = y\,[i]$$

Rearranging,

$$\int_{x\,[i-1]}^{x\,[i]} inc\,[i]\,dx = \frac{((y\,[i] - y\,[i-1] \times (vo - (i-1) \times (nn-a)) + y\,[i-1])}{vo}$$

In the steady state inc [i] is a constant and therefore

$$inc\,[i] = \frac{((y\,[i] - y\,[i-1]) \times (vo - (i-1) \times (nn-a)) + a \times y\,[i-1])}{vo \times (x\,[i] - x\,[i-1])}$$

so that the mean value of the inc [i] may be calculated for a given run for all time intervals x [i] - x [i-1].

In the non steady state, inc [i] is a function of time and $\int_{x\,[i-1]}^{x\,[i]} inc\,[i]\,dx$ gives the total increase in activity for one time interval (referred to the standard volume vo) without any information on the rate inc [i].

Returning to the equation for y [i] then

$$y\,[i] = y\,[i-1] + (vo \times \int_{x\,[i-1]}^{x\,[i]} inc\,[i]\,dx - a \times y\,[i-1])/(vo - (i-1) \times (nn-a))$$

Expanding the numerator vo to vo - (i-1) × (nn-a) + (i-1) × (nn-a) and collecting terms,

$$y[i] = y[i-1] + \int_{x[i-1]}^{x[i]} inc[i]\,dx$$

$$+ \frac{(i-1) \times (nn-a) \times \int_{x[i-1]}^{x[i]} inc[i]\,dx - a \times y[i-1]}{vo - (i-1) \times (nn-a)}$$

As mentioned at the beginning it is necessary to refer all activities to the undisturbed system, therefore $y[i-1] = y[i-1]_{vo} - corr[i-1]$ where the subscript vo refers to the unperturbed activity and the difference is made up by the term $corr[i-1]$.

Therefore,

$$y[i]_{vo} - corr[i] = y[i-1]_{vo} + \int inc[i]\,dx$$

$$+ \frac{(i-1) \times (nn-a) \times \int inc[i]\,dx - a \times y[i-1]}{vo - (i-1) \times (nn-a)}$$

$$- corr[i-1]$$

In the ideal case $y[i]_{vo} = y[i-1]_{vo} + \int inc[i]\,dx$, thus

$$corr[i] = \frac{a \times y[i-1] - (i-1) \times (nn-a) \times \int inc[i]\,dx}{vo - (i-1) \times (nn-a)} + corr[i-1]$$

and $corr[1] = 0.0$

In this form the expression appears in the steady and non steady state diffusion programs (Appendix A.6).

The true curve is obtained by plotting the $y[i]_{vo}$ against the $x[i]$.

APPENDIX A.4

FILM DIFFUSION CORRECTIONS

In the derivation of the expression for the self diffusion coefficient $\bar{D}_A$ it was assumed that diffusion through the membrane was the rate controlling step and that there was no interfacial resistance to diffusion between the membrane and the solution. In a real system however neither assumption is strictly true. The interfacial resistance problem, from which the difficulties arise, has been circumvented by the invention of the 'diffusion layer' concept i.e. that there exists at both membrane faces a layer of average thickness δ which remains unstirred regardless of the efficiency of stirring in the bulk solution. If diffusion through the membrane is faster than through the unstirred films then a concentration gradient is set up in the unstirred layers which lowers the measured diffusion coefficient. By this device, therefore, the assumption of no interfacial resistance is preserved and all effects ascribed to the diffusion layer. If the fluxes through the unstirred films and the membrane are equated, it can easily be shown that for a mobile species i, (1)

$$J_i = - \frac{\bar{D}_i \bar{c}_i}{d.\left(1 + \frac{2\,\bar{D}_i.\bar{c}_i.\delta}{D_i.c_i.d} \right)} \qquad (A.4.1)$$

and hence

$$\bar{D}_{iA} = \frac{\bar{D}_i}{\left(1 + \frac{2\,\bar{D}_i.\bar{c}_i.\delta}{D_i.c_i.d}\right)} \qquad (A.4.2)$$

where D_i, c_i are the diffusion coefficient and concentration of species i in the solution phase.

If $\frac{D_i.c_i.d}{\bar{D}_i\,\bar{c}_i\,\delta} \gg 2$, which is frequently the case for coions and water, then the diffusion process is membrane controlled. If, on the other hand, $\frac{D_i.c_i.d}{\bar{D}_i.\bar{c}_i.\delta} \ll 2$, then the rate controlling step is diffusion through the films. Counterion diffusion usually lies somewhere between the two extremes so that the observed and true membrane diffusion coefficients ($\bar{D}_{1A}$ and $\bar{D}_1$ respectively) may differ significantly. There have been several attempts to correct self diffusion data for the effects of film diffusion or calculate δ directly (2)(3)(4)(5)(6) but the correction applied to observed diffusion coefficients in this work was that of Scattergood and Lightfoot (7). These authors calculate the mean local mass transfer coefficient, k_c, in the boundary layers (where k_c corresponds to the term D_1/δ in equations A.4.1 and A.4.2 above). An important factor in determining the magnitude of k_c is the cell and paddle system geometry and it is therefore necessary to calibrate the diffusion cell before making measurements. This was done by making limiting current measurements with a silver foil cathode in place of the membrane and 0.0005 molar silver nitrate in 1.0 molar sodium nitrate. The current was drawn from an automatic polarograph which gave a linearly increasing voltage with time. A plot of current against time was obtained by monitoring the potential difference across a standard 10 ohm resistor in the circuit with a potentiometric chart recorder. At currents below the limiting current, a linearly increasing plot of current

against time was obtained but when the limiting current was reached the trace levelled off to give a plateau. The experiment was repeated a number of times at stirring speeds of 250, 300, 350, 400, 450, 500 and 550 r.p.m. Overall reproducibility of limiting currents was about 2-3%. The mass transfer coefficient, k_c, is related to the limiting current I by the equation

$$k_c = I^{\infty} / F.(c_1)_b \qquad (A.4.3)$$

where $(c_1)_b$ is the concentration of ion 1 in the bulk solution and the general relation between the mass transfer coefficients and the other variables in the system is

$$\frac{(k_c)_m.B}{D} = A.\,(NL^2\rho/\eta)^q \,.\, (\eta/\rho D)^{\frac{1}{3}} \qquad (A.4.4)$$

where $(k_c)_m$ is the area mean value of k_c

B is the cathode diameter

D is the solvent diffusivity

N is the rate of impeller rotation

L is the impeller diameter

η is the solution viscosity

ρ is the solution density

and A and q are the constants of the system to be determined.

If the logarithms of both sides of equation A.4.4 are taken, the equation may be rearranged to become

$$\log \frac{(k_c)_m.B}{D} = q \log N + \log \left(A.(\eta/\rho D)^{\frac{1}{3}} \,.\, (L^2\rho/\eta)^q\right) \qquad (A.4.5)$$

A plot of log $\frac{(k_c)_m.B}{D}$ versus log N should therefore be a straight line of gradient q. Substitution of q into the constant term yields A. A value for A of 0.26 and, for q, 0.50 were obtained for the cell employed in all self diffusion measurements in this study. Determination of these constants permits the evaluation of k_c for any other membrane and solution from equation A.4.4 and allows a correction for film diffusion effects to be applied.

REFERENCES

1. F. HELFFERICH, "Ion Exchange", McGraw-Hill, New York 1962.

2. M. TETENBAUM AND H.P. GREGOR, J. Phys. Chem., 58 1156 (1954).

3. F. HELFFERICH, Disc. Faraday Soc. 21 83 (1956).

4. A.M. PEERS, Disc. Faraday Soc. 21 124 (1956).

5. M.A. PETERSON AND H.P. GREGOR, J. Electrochem. Soc., 106 1051 (1959).

6. D. MACKAY AND P. MEARES, Kolloid. Z. 167 31 (1959).

7. E.M. SCATTERGOOD AND E.N. LIGHTFOOT, Trans. Faraday Soc. 64 1135 (1968).

APPENDIX A.5

RADIOCHEMICAL DETERMINATION OF UPTAKES

There are two possible approaches to this. The first is to measure the activity of a known volume of radioactive solution before and after placing an inactive membrane into it. The alternative is to equilibrate a membrane in active solution, remove it and place it in a known volume of inactive solution and measure the increase of activity in this solution. For reasons which will be discussed below this second method was employed for both selectivity and coion uptake measurements.

Consider a membrane containing B milliequivalents of ion X. If this is placed in an equilibrium solution containing radioactive X ions an isotopic exchange will occur until the isotopic compositions of X ions in the solution and in the membrane are identical. Samples of the solution will give the counts per minute per milliequivalent of X ions in the solution and hence the membrane (=y).

If the membrane is then blotted and freed from adhering solution films as described in section 3.7, then the total counts per minute in the membrane phase will be B x y. The membrane is then placed in a known volume of an identical inactive solution containing A milliequivalents of X ions.

Total X ion in the system is thus A + B milliequivalents. Isotopic redistribution occurs and the total activity appearing in the solution is $A/(A+B) \times B \times y$. This activity can be determined by taking samples of the solution after equilibration which leaves B as the only unknown.

By an exactly analogous procedure the expression for the total activity

in the solution using the first method is $A/(A+B) \times A \times y$. This method is only suitable where a large reduction in solution counts can be expected, which means that A and B must be at least of the same order with preferably $B \gg A$. Measurement of coion uptakes, where $A \gg B$, is clearly grossly inaccurate by this method and in selectivity measurements even although in some cases A was slightly larger than B, this first method resulted in the subtraction of two large numbers with consequent inaccurate results. The second method was therefore used in all determinations.

APPENDIX A.6 COMPUTER PROGRAMS

```
begin comment Tracer diffusion program Mk 7;
      integer n,f;
      f:=format([sss-d.dddd10-nd]);
      open(20);     open(70);
start:copytext(20,70,[;]);
      n:=read(20);
     begin integer i,qq,h;
           real sx,sy,sxy,sx2,sy2,m,c,d,dy,dm,vo,
                a,nn,avinc,t12,t;
           array x,y,yy,yc,e,corr[1:n],inc[2:n],s[1:9];
           boolean array duff[1:n];
           boolean nohold,decay,ante,dacapo;
           nohold:=decay:=false;
           sx:=read(20);
           sy:=read(20);
           ante:=if sx=sy then false elsetrue;
           if ante then sy:=sy-sx;
           for i:=1 step 1 until n do
           begin    x[i]:=read(20);
                   yy[i]:=read(20);
                   yy[i]:=yy[i]-sx;
                 duff[i]:=false;
           end;
           vo:=read(20);
           nn:=read(20);
            a:=read(20);
           if ante then for i:=1 step 1 until n do
           begin yy[i]:=yy[i]-sy;
                 sy:=sy×(1-a/(vo-ix(nn-a)))
           end;
           if in basic symbol(20)≠152 then decay:=true;
           for i:=1 step 1 until 9 do s[i]:=read(20);
           if in basic symbol(20)=12 then nohold:=true;
           if a=0.0 then
           writetext(70,[[4c]SIMPLE*WITHDRAWAL*SAMPLING[2c]])
           else
           writetext(70,[[4c]WITHDRAWAL/ADDITION*SAMPLING[2c]]);
           if decay then
           begin t12:=read(20);
                   t:=read(20);
                 for i:=1 step 1 until n do
                 yy[i]:=yy[i]/exp(-0.693/t12×(i-1)×t)
           end;
total:     for i:=1 step 1 until ndo y[i]:=yy[i];
           writetext(70,[[2c]*INTERVAL[10s]INC[2c]]);
           sx:=sx2:=0.0;    qq:=0;
           for i:=2 step 1 until n do
           if not(duff[i] or duff[i-1]) then
           begin inc[i]:=(y[i]×(vo-(i-1)×(nn-a))-y[i-1]×
                 (vo-(i-1)×(nn-a)-a))/(x[i]-x[i-1])/vo;
                 write(70,format([ssdd]),i-1);
                 out basic symbol(70,161);
                 write(70,format([dd]),i);  space(70,6);
```

```
            write(7C,f,inc[i]);      newline(7C,1);
            sx:=sx+inc[i];
            qq:=qq+1;
        end;
        avinc:=sx/qq;
        for i:=2 step 1 until n do
        sx2:=sx2+(if not(duff[i] orduff[i-1]) then
         (avinc-inc[i])↑2 else C.C);
        dm:=sqrt(sx2/(qq-1));
        writetext(7C,[[c]AVERAGE*INC*=]);
        write(7C,f,avinc);
        writetext(7C,[[c]STANDARD*DEVIATION*IN*INC*=]);
        write(7C,f,dm);
        corr[1]:=C.C;
        for i:=2 step 1 until n do corr[i]:=axy[i-1]/
        (vo-(i-1)×(nn-a))-avinc×(x[i]-x[i-1])×(i-1)×
        (nn-a)/(vo-(i-1)×(nn-a))+corr[i-1];
        for i:=1 step 1 until n do y[i]:=y[i]+corr[i];
leastsq: sx:=sy:=sxy:=sx2:=sy2:=C.C;     h:=C;
        for i:=1 step 1 until n do ifnot duff[i] then
        begin sx:=sx+x[i];
              sy:=sy+y[i];
             sxy:=sxy+x[i]×y[i];
             sy2:=sy2+y[i]↑2;
             sx2:=sx2+x[i]↑2;
               h:=h+1;
        end;
        d:=h×sx2-sx↑2;
        m:=(h×sxy-sx×sy)/d;
        c:=(sx2×sy-sx×sxy)/d;
        for i:=1 step 1 until n do
        if not duff[i] then yc[i]:=m×x[i]+c;
       dy:=sy2+h×c↑2+m↑2×sx2-2×(c×sy+m×sxy-m×c×sx);
       dm:=sqrt(h×dy/(h-2)/d);
        d:=sqrt(dy×sx2/(h-2)/d);
        for i:=1 step 1 until n do
        if not duff[i] then e[i]:=y[i]-yc[i];
        writetext(7C,[[4c]M*=]);     write(7C,f,m);
        writetext(7C,[[3s]STANDARD*DEVIATION*IN*M*=]);
        write(7C,f,dm);
        writetext(7C,[[2c]C*=]);
        write(7C,f,c);
        writetext(7C,[[3s]STANDARD*ERROR*IN*C*=]);
        write(7C,f,d);
        writetext(7C,[[2c]RMS*ERROR*IN*Y*=]);
        write(7C,f,sqrt(dy/(h-2)));
        writetext(7C,[[3c5s]Y*INIT[9s]CORR[10s]Y*OBS[8s]
        Y*CALC[7s]DEVIATION[2c]]);
        for i:=1 step 1 until n do if not duff[i] then
        begin write(7C,f,  yy[i]);
              write(7C,f,corr[i]);
              write(7C,f,   y[i]);
             write(7C,f,  yc[i]);
```

```
                write(7C,f,   e[i]);      newline(7C,1);
            end;
            d:=mxvoxs[1]xs[2]/(s[3]xs[4]xs[5]x6C);
            writetext(7C,[[2c]DIFFUSION*COEFF*D1A*=**]);
            write(7C,f,d);
            if not nohold then
            begin writetext(7C,[[2c]HOLD*UP*TIME*(MIN)*=**]);
            write(7C,f,-c/m);
            writetext(7C,[[2c]HOLD*UP*TIME*DIFF*COEFF*=**]);
                write(7C,f,-s[2]↑2xm/(cx36C));
            end;
            dm:=C.11733xsqrt(s[9]x5.29xs[7]/s[8])x
                (s[8]xs[6]↑2/s[7])↑(1/3);
            writetext(7C,[[4c]SCATTERGOOD/LIGHTFOOT*CORRECTION[2c]
            MASS*TRANSFER*COEFF*=**]);
            write(7C,f,dm);
            writetext(7C,[[2c]DIFFUSION*COEFF*D1*=**]);
            write(7C,f,d/(1-(2xdxs[3]/(s[2]xdmxs[1])))));
again:      if in basic symbol(2C)=12 then goto newdata;
            dacapo:=readboolean(2C);
            if in basic symbol(2C)=152 then for i:=read(2C)
            while in basic symbol(2C)≠13 do duff[i]:=true;
            if dacapo then writetext(7C,[[6c]TOTAL*]) else
            writetext(7C,[[6c]LEAST*SQUARE*]);
            writetext(7C,[RECALCULATION*OMITTING*POINTS]);
            for i:=1 step 1 until n do
            if duff[i] then write(7C,format([snd]),i);
            newline(7C,2);
            if dacapo then goto total else goto leastsq;
newdata:    if in basic symbol(2C)=142 then goto start;
            close(2C);   close(7C)
        end
end→
```

```
begin comment Non steady state Fickian diffusion program;
      integer f,o,p;
      real e;
      f:=format([5s-d.dddd10-nd]);
      e:=ln(10.0);
      open(20);      open(70);
again: copytext(20,70,[;]);
      p:=read(20);
      o:=read(20);
      begin integer i,m,ma,mc,md;
            real vo,nn,a,sx,sy;
            array ab,or,orc,err[1:o];
            boolean skip,dil,first;
            first:=true;
            skip:=if in basic symbol(20)=152 then
                  false else true;
            if skip then
            begin sx:=0.0;
                  goto intake
            end;
            sx:=read(20);
            sy:=read(20);
            dil:=if sx=sy then false else true;
            if dil then sy:=sy-sx;
intake:     for i:=1 step 1 until o do
            begin ab[i]:=read(20);
                  or[i]:=read(20);
                  or[i]:=or[i]-sx
            end;
            if skip then goto fit;
            vo:=read(20);
            nn:=read(20);
             a:=read(20);
            if dil then for i:=1 step 1 until o do
            begin or[i]:=or[i]-sy;
                  sy:=sy×(1-a/(vo-i×(nn-a)))
            end;
            writetext(70,[[2cs]INTERVAL[10s]TOTAL*INC[2c]]);
            for i:=2 step 1 until o do
            begin err[i]:=((or[i]-or[i-1])×(vo-(i-1)×(nn-a))+
                        a×or[i-1])/vo;
                  write(70,format([ssdd]),i-1);
                  out basic symbol(70,161);
                  write(70,format([dd]),i);
                  space(70,6);
                  write(70,f,err[i]);   newline(70,1)
            end;
            orc[1]:=0.0;
            for i:=2 step 1 until o do orc[i]:=a×or[i-1]/
            (vo-(i-1)×(nn-a))-err[i]×(i-1)×(nn-a)/(vo-(i-1)×
            (nn-a))+orc[i-1];
            for i:=1 step 1 until o do or[i]:=or[i]+orc[i];
            writetext(70,[[2c]POINT[10s]VOL*CORR[2c]]);
```

```
            for i:=1 step 1 until o do
            begin write(7C,format([ssdd]),i);   space(7C,5);
                  write(7C,f,orc[i]);    newline(7C,1)
            end;

fit: m:=p+1;
     ma:=p;
     mc:=m+1;
     md:=mx2-1;
      begin integer j,k,l,n,mn,ka,mb,am;
            real ans,bans,b,in,q;
            array c,d[1:m,1:m],t,x[1:m],detr[1:mc],keep[1:md];
            procedure ASSIGN(n);
            value n;
            integer n;
            begin mn:=n+1;
                  for i:=1 step 1 until n do
                  begin j:=mn-i;
                        if i≤m and j≤m then c[i,j]:=keep[n]
                  end
            end ASSIGN;
            for i:=1 step 1 until  m do   t[i]:=C.C;
            for i:=1 step 1 until md do keep[i]:=C.C;
            for i:=1 step 1 until  o do
           begin in:=1.C;
                  for j:=1 step 1 until md do
                  begin keep[j]:=keep[j]+in;
                        if j≤m thent[j]:=t[j]+or[i]xin;
                        in:=inxab[i]
                  end
            end;
            for k:=1 step 1 until md do ASSIGN(k);
           ans:= C.C;
           for i:=1  step 1 until m do ans :=ans+(if c[i,i]>C.C
           then ln(c[i,i])/e else if c[i,i] =C.C then C.C
           else ln(abs(c[i,i]))/e);
           am:=m;
           ans:=ans/am;
           bans:= 1C.C↑ans;
           for i:=1 step 1 until m do
                begin
                t[i]:=t[i]/bans;
                for j:=1 step 1 until mdo
                c[i,j]:= c[i,j]/bans;
                end;
           for j:=1 step 1 until  mc do
                begin
                for i:=1 step 1 until m do
                for k:= 1 step 1 until m do
                d[k,i]:=c[k,i];
                b:=1.C;
                mb:=j-1;
                if mb≠C then for k:=1 step 1 until m do
                d[k,mb]:=t[k];
```

```
      for k:=1 step 1 until ma do
                begin
                ka:=k+1;
              if d[k,k]=C.C then goto P86;
          P8C: b:=d[k,k]×b;
                q:=d[k,k];
                for l:=k step 1 until m do d[k,l]:=d[k,l]/q;
                for l:=ka step 1 until m do
                begin
                a:=d[l,k];
                for n:=k step 1 until m do
                d[l,n]:= d[l,n]-d[k,n]×a;
                end;
          for l:=ka step 1 until m do d[k,l]:=C.C;
          goto out;
      P86: for i:=ka step 1 until m do if d[k,i]≠C.C then
          begin
          b:= -b;
          for l:=k step 1 until m do
          begin
          in:= d[l,k];
          d[l,k]:=d[l,i];
          d[l,i] := in;
          end;
          goto P8C;
      end;
      detr[j]:=C.C;
      goto fin;
out:  end;
      detr[j]:=d[m,m]×b;
fin:  end;
       for j:=2 step 1 until mc do x[j-1]:=detr[j]/detr[1];
       writetext(7C,[[2c]ORDER*OF*FIT*=*]);
       write(7C,format([dd]),p);
       writetext(7C,[[4c]POWER*OF*A[5s]COEFFICIENT[2c]]);
       for i:=1 step 1 until m do
       begin write(7C,format([ssssdd]),i-1);
             space(7C,4);
             write(7C,f,x[i]);
             newline(7C,1)
       end;
       for i:=1 step 1 until o do
       beginorc[i]:=x[m];
             for j:=ma step -1 until 1 do orc[i]:=x[j]+
             orc[i]×ab[i];
             err[i]:=or[i]-orc[i]
       end;
       writetext(7C,[[2c6s]ABSCISSA[11s]ORDINATE[11s]
       CALC*ORDINATE[11s]DEVIATION[2c]]);
       for i:=1 step 1 until o do
       begin write(7C,f,ab[i]);      space(7C,3);
             write(7C,f,or[i]);      space(7C,3);
             write(7C,f,orc[i]);     space(7C,8);
```

```
                write(7C,f,err[i]);   newline(7C,1)
            end;

                if notfirst then
                begin sy:=x[2];   goto finale
                end;
                for i:=1 step1 until o do
                begin err[i]:=x[m]×(m-1);
                      for j:=ma step -1 until 2 do
                      err[i]:=x[j]×(j-1)+err[i]×ab[i];
                      or[i]:=ln(err[i]×sqrt(ab[i]));
                      ab[i]:=1/ab[i]
                end
            end;
            p:=1;
            first:=false;
            writetext(7C,[[4c]ORDINATE*IS*NOW*LN(DP/DT×T↑C.5)[c]
            ABSCISSA*IS*NOW*1/T[4c]]);
            goto fit;
finale:     sx:=read(2C);
            sx:=sx×sx;
            writetext(7C,[[6c]DIFFUSION*COEFFICIENT*(CM2SEC-1)*=*])
            write(7C,f,-sx/(sy×24C));
        end;
        if in basic symbol(2C)=142 then gotoagain;
        close(2C);     close(7C)
end→
```

```
begin comment Transport numbers from self diffusion flux
              and flux with or against the current;
      integerz,l,f;
      real ta,tb,tc,tg,amp,jo,jg,c,d,ratio,x;
      boolean with,bar;
      f:=format([sss-d.dddd10-nd]);
      open(2C);      open(7C);
start:copytext(2C,7C,[;]);   inbasic symbol(2C);
      if in basic symbol(2C)=152 then with:=true else with:=false;
      bar:=false;
        z:=read(2C);
      amp:=read(2C);
       .c:=read(2C);
        d:=read(2C);
       jo:=read(2C);
       jg:=read(2C);
       tg:=read(2C);
        l:=read(2C);
        x:=if in basic symbol(2C)=152 then 1.C10-3 else read(2C);
       jo:=jo×c/d;
       jg:=jg×c/d;
       c:=9.649104×z×jo/amp;
        d:=amp/z/jg/9.649104;
      if with then ta:=1/d else ta:=if in basic symbol(2C)=152
       then read(2C) else1.C;
       tb:=C.C;
      writetext(7C,[[cc]CYCLE[3s]T*GIVEN[7s]T*CALC[8s]RATIO[cc]]);
        z:=C;
loop: if z=l then goto stop;
        z:=z+1;
      if with then
      begin tc:=-c×ln(1-d×tg);
            ratio:=tg/tc;
      end else
      begin tc:=c×ln(1+d×tg);
            ratio:=tc/tg;
      end;
      write(7C,format([ssdd]),z);
      write(7C,f,tg);
      write(7C,f,tc);
      write(7C,f,ratio);
      newline(7C,1);
retest: if abs(ratio-1.C)<x then gotoout;
      if ratio>1.C thentb:=tg else ta:=tg;
      tg:=(ta+tb)/2;
      goto loop;
stop: writetext(7C,[[cc]NOT*CONVERGENT*WITHIN*CYCLE*LIMIT[cc]]);
      goto fin;
out: if bar then goto fin;
      x:=x/1C;
```

```
      bar:=true;
      l:=l+1;
      writetext(7C,[DISCRIMINATION*INCREASED*BY*TEN[c]]);
      goto retest;
fin:  if in basic symbol(2C)=142 then
      begin bar:=false;   goto start
      end;
      close(2C);      close(7C);
end→
```

```
begin comment Glueckauf permeability program;
      real D,ko,z,nug,zg,ms,mup,Io,Mcon,M,alpha,yn,fn,P,
           phi,x,int,f,fa,lim,step,xx,a,k;
      integerfor;
      boolean up,one;
      procedure INTSTEP(y,f,x,h,AUX);
      value h;
      real y,f,x,h;
      procedure AUX;
      begin
           real q,w;
           AUX(f,x);
           q:=h×f;
           y:=y+0.5×q;
           x:=x+0.5×h;
           AUX(f,x);
           w:=0.292893218813×(h×f-q);
           y:=y+w;
           q:=2.0×w + 0.7071067811865×q;
           AUX(f,x);
           w:=1.7071067811865×(h×f-q);
           y:=y+w;
           q:=2.0×w - 0.7071067811865×q;
           x:=x+0.5×h;
           AUX(f,x);
           y:=y+0.333333333333×(0.5×h×f-q);
     end INTSTEP;
      procedureDERIV(f,x);
      value x;
     real x,f;
      begin real P2;
            if     up and     one then P2:=exp(x)+phi;
            if     up and not one then P2:=1-exp(x);
            if not up and     one then P2:=phi-exp(x);
            if not up and not one then P2:=exp(x);
            P2:=(k×P2)↑a;
            P2:=D×(-P2/ms+sqrt(P2↑2/ms/ms+4.0×alpha↑2))/2;
            f:=3.0×P×(P2-P)/(2.0×P+P2);
      end DERIV;
      procedure DERIVA(fa,M);
      value M;
      real M,fa;
      begin
           fa:=ko×M↑(-z);
      end DERIVA;
      open(20);     open(70);
again: copytext(20,70,[;]);
      for:=format([d.dd10-ndc]);
test(0);
               D:=read(20);
              ko:=read(20);
               z:=read(20);
             nug:=read(20);
```

```
              zg:=read(2C);
              ms:=read(2C);
             mup:=read(2C);
              Io:=read(2C);
            Mcon:=read(2C);
             int:=read(2C);
             lim:=read(2C);
            step:=read(2C);
              up:=readboolean(2C);
cycle:     alpha:=(nugxmup/(koxIo))↑(1.C/(2.C-z))/(nugxms);
           yn:=Mcon/(nugxzgxalphaxms);
           fn:=C.5x(-yn+sqrt(yn↑2.C+4.C));
           P:=Dxalphaxfn;
           a:=1.C/(1.C-z);
           k:=(1.C-z)/ko;
           phi:=M:=C.C;
           forM:=M while M≤Mcon do
           INTSTEP(phi,fa,M,int,DERIVA);
           writetext(7C,[MOLALITY*OF*MOST*CONTINUOUS*REGION*=**]);
           write(7C,for,Mcon);
           writetext(7C,[VALUE*OF*PHI*FOR*THIS*REGION*=**]);
           write(7C,for,phi);
           if up thenxx:=ln(1.C-phi) else xx:=ln(phi);
            x:=-12.C;
            one:=true;
            for x:=x while x+C.1≤xx do
           INTSTEP(P,f,x,C.1,DERIV);
           one:=false;
           x:=xx;
           for x:=x while x+C.1≤C.C do
           INTSTEP(P,f,x,C.1,DERIV);
test(C);
       writetext(7C,[[c]PERMEABILITY*COEFF*=**]);
           write(7C,for,P);
           newline(7C,2);
           writetext(7C,[GLUECKAUF*DIFFUSION*COEFF*=**]);
           write(7C,for,Pxms/mup);
           Mcon:=Mcon+step;
           if Mcon<lim then
           begin writetext(7C,[[2c]MCON*=**]);
                 write(7C,for,Mcon);
                 int:=Mcon/1C;
                 gotocycle
           end;
           if in basic symbol (2C) =142 then goto again;
     close(2C);     close(7C);
end→
```